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OCCLUDED GASES IN FERROUS ALLOYS.*

BY

GELLERT ALLEMAN,

Professor of Chemistry, Swarthmore College, Pa.,
Member of the Institute,

AND

CHARLES J. DARLINGTON,

Department of Chemistry, Swarthmore College.

PART I.—HISTORICAL.

ALL chemists are familiar with the epoch-making discoveries of Thomas Graham, the distinguished Scottish chemist. He is probably best known in consequence of his classical researches on the phosphoric acids and on the diffusion of gases and liquids. Having succeeded Sir John Herschel as Master of the English Mint, he proved to be an able administrator. He was also distinguished as a metallurgist, and in 1866 made the first published contribution on what we to-day term "occluded gases."[1] Previous to this time Sir Henry Bessemer[2] observed that the violent bubbling in molten steel during the cooling of the metal was due to the evolution of large quantities of carbon monoxide. Graham, however, was not aware of the importance of this observation. His work was suggested by an article published by

* Presented at the stated meeting of the Institute, held Wednesday, October 17, 1917.

[1] *Proc. Roy. Soc.*, 15, 1866–67, pp. 502–503.

[2] *Jour. Iron and Steel Inst.*, 1881, 1, pp. 197–199.

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Deville and Troost[3] (1863) on "The Diffusion of Hydrogen Through Iron." Their results are summarized as follows:

"There may be imagined as existent in metals a new kind of porosity, the minuteness of which far exceeds that of charcoal and earthenware. This porosity is a physical phenomenon brought about by heat through an enlargement of the interstices between molecules. Although it is supposed to be a property of all metals, iron and platinum, at low temperatures, do not possess a porosity sufficient to permit of the diffusion of gases through them."

Graham concluded that if hydrogen possessed the property of diffusing through iron, it was more than likely that a certain amount of hydrogen would be absorbed by the iron during diffusion. The gas so absorbed he designated as "occluded" gas, and this term has since come into general use as being applicable to all gases so held. In his first experiment Graham used a piece of meteoric iron, weighing 43.2 grammes. After thoroughly cleaning the sample by washing it in a solution of hot potassium hydrate and subsequently in hot water, he dried it and placed it in a porcelain tube connected to a Sprengel mercury vacuum pump. The tube was then heated to redness, by means of a gas flame, and the quantity of gas which was evolved was measured at various periods. The results obtained were:

Time in minutes	Volume in cubic centimetres
35	5.38
Next 100	9.52
Last 20	1.63
Total 155	Total 16.53

The first portion of gas was burned and gave a flame similar to that of hydrogen. Analysis of the second portion showed it to have the following composition:

	Per Cent.
Hydrogen	85.65
Carbon monoxide	4.46
Nitrogen	9.86

From these data, and the specific gravity of the sample, it was calculated that one volume of iron evolved 2.85 volumes of gas.

[3] *Compt. rend.*, 57, 1863, pp. 965–967.

The only conclusion which Graham drew from the above results was that the atmosphere through which the meteor had passed consisted largely of hydrogen. Recent investigations seem to indicate that the atmosphere surrounding the earth to a height of from seventy-five to one hundred miles contains large amounts of hydrogen. The following table illustrates the supposed hydrogen content of the earth's atmosphere at various altitudes:

Height in kilometres	Per cent. hydrogen
140	99.15
130	99.00
120	98.74
110	98.10
100	95.58
90	88.28
80	64.70
70	32.61
60	10.68
50	2.76
40	0.67
30	0.16
20	0.04
15	0.02
11	0.01
5	0.01
0	0.01

REFERENCES ON DISTRIBUTION OF HYDROGEN IN THE ATMOSPHERE.

Ferrel: "Recent Advances in Meteorology," 1886, p. 37.
Hahn: "Lehrbuch der Meteorology," 1906, pp. 5–8.
v. dem Borne: *Physik. Zeitschr.*, 11 (1910), 11, p. 483.
W. J. Humphreys: *Bull. Mount Weather Obs.*, 1909, pp. 66–69.
JOURNAL OF THE FRANKLIN INSTITUTE, September, 1917, p. 388.

A. Wagener[4] gives a supplementary table, which differs from the above only in that these latter observations were carried out at higher altitudes. It is interesting to note that the figures thus obtained show a decrease in the hydrogen content of the atmosphere at altitudes over 150 kilometres. This, however, does not detract from the importance of these observations with reference to the subject in question, for, from a consideration of these results, it follows that the meteor probably acquired its hydrogen after passing from the ether into the atmosphere of the earth.

Graham's interest was considerably aroused by the results of his work on meteoric iron, and he sought to determine whether

[4] A. Wagener: *Z. Anorg. Chem.*, **75**, 1912, pp. 107–131.

other ferrous materials were capable of absorbing gases. Employing the same apparatus and methods detailed in his first investigation, he heated 23.5 grammes of horseshoe nails. The amounts of gas produced and the analysis of the same are given in tabular form.

Time in Minutes	Volume in c. c.	Per cent. Hydrogen	Per cent. Carbon Monoxide	Per cent. Carbon Dioxide	Per cent. Nitrogen
First 150	5.40	35.0	50.3	7.7	7.0
Next ... 120	2.58	21.0	58.0	0.0	21.0
Total . 270	7.98				

It was calculated that one volume of metal yielded 2.66 volumes of gas.

While not directly connected with the subject outlined, we must refer to one of Graham's most interesting experiments. He made a palladium wire cathode in an acidulated solution. The palladium absorbed the H which migrated to it, and the wire, which originally had a length of 609.58 mm., attained a length of 619.34 mm.; in other words, the occlusion of H increased the length of this wire 9.77 mm.

Upon heating this palladium wire in a vacuum its length decreased to 600.18 mm., or 9.4 mm. less than its original length before it was made cathode.

Graham[5] next conducted a number of experiments investigating the amounts of hydrogen and carbon monoxide absorbed by palladium, platinum, gold, silver, antimony, and iron. His method consisted in (1) heating the metal in a vacuum in order to drive off the gas originally present; (2) then saturating the metal with hydrogen or carbon monoxide; (3) allowing it to cool, and (4) finally heating it again to determine the amount of gas evolved.

In performing these experiments no difficulty was experienced in obtaining satisfactory results except in the case of iron, from which it was found to be practically impossible to set free all of the gas originally occluded. Graham made no records of definite temperatures attained, merely stating that the porcelain tubes in which the determinations were made were heated to redness. In subsequent experiments Graham heated iron wire having a diameter of 0.4 mm. In a series of three experiments he was unable to remove all of the occluded gases from the wire.

[5] *Proc. Roy. Soc.*, 16, 1867–1868, pp. 422–427, and *Jour. of the Chem. Soc.*, 20, 1867, pp. 257–292.

In his first experiment on wire he used 46 grammes of the wire mentioned. This, when subjected to several periods of heating, yielded, for each volume of iron, 7.94 volumes of gas, and the evolution had not ceased when the records given below were completed.

RESULTS OF EXPERIMENT No. 1

	Time in Minutes	Volume in c. c.	Per cent. Carbon Dioxide	Per cent. Carbon Monoxide
First	15	15.60	22.4	
Next	15	7.17	7.2	
Next	30	10.40		66.0
Next	30	8.16	1.4	
Last	30	5.52	0.5	
Total	120	46.85	31.5	66.0

In the second test a glass tube was employed, as Graham was in doubt as to whether the porcelain tube before employed was free from porosity. Thirty-five grammes of iron, on being heated for one hour, evolved 29.8 cubic centimetres of gas, of which 4.44 cubic centimetres was carbon dioxide, and the remainder mostly carbon monoxide, with traces of hydrogen and methane. One volume of iron yielded 7.27 volumes of gas.

In the third experiment 39 grammes of wire evolved, in seven hours, 63.10 cubic centimetres of gas, or one volume of iron produced 12.55 volumes of gas.

The iron left in the glass tube was then saturated with hydrogen and it was found that 0.42 volume was absorbed. On treatment with carbon monoxide one volume of the metal took up 4.15 volumes of that gas.

As a further experiment a piece of soft iron was allowed to remain in dilute acid for a time. As a result of this treatment 0.57 volume of hydrogen was occluded in the metal. In commenting on the results of these three experiments Graham advanced the theory that hydrides of iron were formed, and he considers it improbable that such large quantities of hydrogen could have been held in the gaseous state.

Simultaneously with the researches of Graham in England, Cailletet,[6] in France, was making observations on the gases evolved from iron during fusion. Employing two different samples of iron, he obtained gases of the following composition:

[6] *Compt. rend.*, 61, 1865, pp. 850–852.

Gas	Sample No. 1 Per cent.	Sample No. 2 Per cent.
Hydrogen	33.7	38.6
Nitrogen	57.9	49.2
Carbon monoxide	8.4	12.2

Cailletet, however, was unable to duplicate his results, and discontinued the investigation.

Troost and Hautefeuille,[7] some years late, observed that when metals were heated and then allowed to cool, bubbles often appeared on the surfaces. They concluded that these bubbles were formed by gases which dissolved at high temperatures, and which were forced out of solution on cooling. In support of this theory of Troost and Hautefeuille, cast iron was heated in an atmosphere of hydrogen. Although at first no disturbance was noticed, when the pressure was suddenly lowered the evolution of gas was evident by the appearance of numerous bubbles. When allowed to cool and solidify, the surface of the iron was found to be very rough. It was thought likely, however, from comments previously made by Graham and by Cailletet, that certain amounts of gases were occluded at ordinary temperatures. In a series of experiments attempting to liberate the occluded gas, the investigators proceeded as follows:

A block of iron weighing 500 grammes was heated, in an evacuated porcelain tube, at 800° C. for 134 hours, and saturated, first, with hydrogen for 48 hours, and finally with carbon monoxide for 166 hours. After saturation the metal was reheated in order to determine how much of the gases had been absorbed. The accompanying tables give the results of these procedures:

EXPERIMENT NO. 1.—*Cast Iron*

Gas	Originally present		After saturation			
			In hydrogen		In carbon monoxide	
	Cubic centimetres	Per cent.	Cubic centimetres	Per cent.	Cubic centimetres	Per cent.
Carbon dioxide	0.6	3.59	0.0	0.00	0.0	0.00
Carbon monoxide	2.8	16.76	1.1	2.36	14.7	86.98
Hydrogen	12.3	74.07	44.0	94.42	1.5	8.87
Nitrogen	1.0	5.58	1.5	3.22	0.7	4.15
Total	16.7	100.00	46.6	100.00	16.9	100.00

[7] *Compt. rend.*, 76, 1873 pp. 482–485, 562–566, and *Annal. de Chem. et de Phys.*, 7, 1876, pp. 155–177.

EXPERIMENT NO. 2.—*Steel.*

Gas	Originally present		After saturation			
			In hydrogen		In carbon monoxide	
	Cubic centimetres	Per cent.	Cubic centimetres	Per cent.	Cubic centimetres	Per cent.
Carbon dioxide....	.05	2.27	0.0	00.00	00.00	00.00
Carbon monoxide..	1.40	63.65	.9	11.53	2.0	62.5
Hydrogen.....	.50	22.72	6.4	82.05	.8	25.0
Nitrogen.....	.25	11.36	.5	6.42	.4	12.4
Total.....	2.20	100.00	7.8	100.00	3.2	99.9

EXPERIMENT NO. 3.—*Wrought Iron*

Gas	Originally present		After saturation			
			In hydrogen		In carbon monoxide	
	Cubic centimetres	Per cent.	Cubic centimetres	Per cent.	Cubic centimetres	Per cent.
Carbon dioxide....	2.2	11.89	0.0	00.00	00.00	00.00
Carbon monoxide..	10.8	58.38	.6	4.31	13.7	97.85
Hydrogen.....	4.4	23.78	10.0	71.94	.2	1.43
Nitrogen.....	1.1	5.95	3.3	13.75	.1	.72
Total.....	18.5	100.00	13.9	100.00	14.00	100.00

It is to be noted that in all three cases the carbon dioxide originally present is missing from the results of analyses made after the second heat. This shows one of two things: either that the carbon dioxide was completely driven off during the first heat, or that the part remaining was decomposed to carbon monoxide and oxygen. Since, however, Troost and Hautefeuille do not describe their analytical methods, we do not know whether any attempts were made to determine the oxygen content of the gas, and therefore cannot say with certainty which of the above explanations accounts for the disappearance of the carbon dioxide.

As to the order in which the gases were driven from the metal, Troost and Hautefeuille expressed the opinion that the oxides of carbon came off first, hydrogen showing a stronger affinity for the iron. The large volume of the test piece used prevented their determining whether all the gas had been driven off.

From the results of their work Troost and Hautefeuille arrived at several conclusions, which may be summarized as follows:

1. Whenever iron is held in a molten condition in contact with silica and silicates, carbon monoxide is produced by the action of iron carbide on the silica and silicates.

2. Molten iron dissolves appreciable quantities of hydrogen, but this amount is dependent on the impurities present, for silicon and phosphorus greatly diminish, while manganese greatly increases the quantity of hydrogen absorbed.

3. Carbon monoxide is much less soluble in iron than is hydrogen, and is rendered even less soluble by the presence of manganese.

4. Cast iron on solidification has been found to contain gases which may be expelled by heating the metal to 800° C.

5. Steel dissolves considerably less carbon monoxide and more hydrogen than does cast iron.

6. Soft iron, on the other hand, dissolves appreciably more carbon monoxide, which it likewise retains more tenaciously.

Upon continuing to follow in historical sequence the experiments conducted on the subject of occluded gases, it is found that John Parry[8] published the next series of investigations. In making his determinations Parry used three different kinds of tubes:

"1. One porcelain tube was enclosed within another, the intervening space being filled with a mixture of fire-clay and blast-furnace slag. Upon heating the empty tube for 48 hours under a vacuum there was evolved only 1 to 1.5 c.c. of gas, consisting mostly of air.

"2. A porcelain tube was painted with water-glass and rolled in finely powdered aluminous iron ore until uniformly coated.

"3. A glass tube enclosing a white clay tube with clay moulded over withstood a heat of about 1000° C. This latter type of tube was finally selected as being best adapted to the work for which it was intended."

The results of Parry's first series of experiments are summarized in the table on page 9.

All experiments at higher temperatures were unsatisfactory as the tubes melted. It was observed that the gas evolved at the lowest red heat consisted almost entirely of hydrogen, and that when the temperature was raised the percentage of carbon monoxide increased.

[8] *Jour. Iron and Steel Inst.*, 1872, **2**, pp. 238–247; 1873, 1, p. 430; 1874, 1, pp. 92–102; 1881, 1, pp. 183–194.

COMPOSITION OF GAS.

Material	Gas evolved per cubic centimetre of metal	Carbon dioxide	Carbon monoxide	Hydrogen	Nitrogen	Total
50 g. of Spiegeleisen (heated for 3 hours)	2 c.c.	0.942	17.87	81.105	.....	99.917
50 g. of common white pig iron (heated for 6.5 hours)	2 c.c.	6.80	2.32	84.00	6.88	100.00
37 g. of good wrought iron (heated for 2 hours)	2 c.c.	9.92	34.26	54.10	1.718	99.998
4.75 g. of gray pig iron (heated for 2 hours)	2.1 c.c.	1.6	5.2	89.7	3.25	99.75
10 g. of soft steel (heated for 2 hours)	13 c.c.	16.55	24.352	52.61	6.488	100.00

Parry repeated some of the experiments conducted by Graham on saturating iron with hydrogen and carbon monoxide. With carbon monoxide he obtained results which coincided almost exactly with those of Graham; but with hydrogen he got figures much higher than Graham's. Parry found that one volume of iron would absorb 4½ volumes of carbon monoxide and from 20 to 22 volumes of hydrogen. There was a very distinctive feature about the procedure used by Parry in these determinations. He measured the gas which was absorbed by the iron, whereas Graham had measured the gas indirectly by determining the volume evolved on heating the metal a second time.

In Table I, page 170, are tabulated a number of Parry's results obtained in a later series of investigations, in which he heated gray pig iron in a vacuum. From these data Parry concluded that the carbon monoxide was not present as such in the iron, but was the result of a chemical reaction between the porcelain tube and the carbon compound of the metal. This conclusion was based on the fact that when certain of the test samples were wrapped in platinum Parry got results much lower than when the samples were allowed to remain in contact with the tube.

In the second experiment a sample of gray pig iron evolved 58 volumes of hydrogen, while the same metal, when tested as previously described, was found to have taken up only 22 volumes. Parry was at a loss to account for this discrepancy.

About seven years after he had obtained the results recorded

TABLE I.

Gases Evolved from Gray Pig Iron Heated in Vacuo—Parry.

Sp. gr. of Fe—6.666	Hours	Gas c.c.	Composition, per cent.			1 vol. of Fe gives H_2 vols.	1 vol. of Fe gives CO vols.	Total volumes of H_2 +CO	Vols. per hr. H_2	Vols. per hr. CO	Remarks
			CO_2	CO	H_2						
10 G. red heat.....	7.5	36	3.49	30.37	66.13	16.72	7.28	24.0	2.23	.97	Kept warm one day, vacuum maintained.
10 G. again red heat.....	10	31	....	36.00	64.10	17.03	9.57	26.60	1.703	.957	
10 G. again red heat.....	9	19	....	43.80	55.90	7.09	9.51	12.60	.789	.611	Cooled to lowest red heat, 12 hours; good vacuo.
10 G. again red heat.....	10.5	21.5	....	46.20	52.78	7.70	6.60	14.3	.733	.638	
10 G. again red heat.....	14	22.7	....	38.20	61.34	9.34	5.77	15.1	.667	.412	
10 G. again red heat.....	9	18.7	....	38.20	61.20	7.67	4.73	12.4	.844	.527	
10 G. again white heat...	16	34.1	....	68.10	31.89	7.21	15.39	22.6	.450	.962	Gas still evolved.
4½ G. red heat.....	19	11.11	2.00	30.00	66.16	11.55	4.95	16.5	.592	.278	
4½ G. white heat.....	9	23.35	....	57.10	43.90	14.80	19.70	34.5	1.646	2.186	
4½ G. white heat.....	9.5	16.0	....	52.00	47.00	23.43	25.37	48.8	1.340	1.460	Evolution slackens at white heat.
4½ G. white heat.....	8	17.0	....	.....	.....	.....	.....	.....	.....	.....	
4½ G. white heat.....	7	16.0	....	64.00	35.50	8.53	15.17	23.7	2.180	1.210	
Total from 10 G.....	76	133	....	.....	.....	72.76	54.84	127.6	.....	.....	Iron unchanged; still gray.
Total from 4½ G.....	52.5	83.46	....	.....	.....	58.31	65.19	123.5	.....	.....	
5.16 G. wrapped in pt. dull red heat	9	34.4	Trace	26.00	74.00	37.00	7.60	44.6	3.67	1.289	
5.16 G. red heat.....	15	18.2	.50	25.82	74.00	17.60	6.00	23.6	1.166	.404	
5.16 G. high red heat....	12	17.4	.70	13.00	86.00	20.35	2.25	22.6	1.636	.244	
Total.....	36	70.0	....	.....	.....	74.95	15.95	90.80	.....	.....	
3.33 G. wrapped in pt. red heat	12	36.0	1.00	19.00	78.00	58.30	13.70	72.00	4.740	1.200	
3.33 G. full red heat.....	5	26.0	....	20.00	80.00	41.60	10.40	52.00	8.320	2.080	
3.33 G. full heat of furnace	42	35.2	....	33.30	66.00	46.90	23.40	70.30	1.102	.560	
Total.....	59	97.2	....	.....	.....	146.80	47.50	194.30	.....	.....	Outer tube melted; inner tube O. K.
Again.....	14.5	23.4	....	17.80	81.00	38.00	8.33	46.80	2.64	.58	Gas still evolved; Fe unchanged.

in the accompanying table, Parry[9] published the results of another series of experiments on the same subject. In order to ascertain whether or not he was correct in believing that iron carbide acted on porcelain, he analyzed some iron both before and after heating it for 48 hours in a porcelain tube. The results of this work are given below:

Contents of tube	Per cent. silicon	Per cent. carbon
Original sample	0.87	5.32
Sample after 24 hours in tube	1.07	3.90
Globule imbedded in tube	3.40	....
Cast steel	0.10	1.54
After 24 hours' fusion in Hessian crucible	0.26	0.74
After 2 hours' fusion in silicious crucible	0.80	0.70

Since the percentage of carbon is shown to have decreased, it was concluded that a large error was introduced in allowing the test samples to come in contact with porcelain, therefore, in all later work, crucibles of lime and of magnesia were used. Proceeding with his work, Parry obtained much larger quantities of gas than before. Gray iron heated for 165 hours evolved 205 times its own volume of hydrogen and 135 times its own volume of carbon monoxide. During the first 128 hours the ratio of hydrogen to carbon monoxide was one part of hydrogen to 0.9 part of carbon monoxide. During the last 36 hours the ratio was one part of hydrogen to 0.213 part of carbon monoxide. When heated in hydrogen, the iron (free of hydrogen and carbon monoxide) was found to absorb 20 volumes; when heated in carbon monoxide, the same iron did not absorb an appreciable amount of the gas, but after remaining in contact with the iron at red heat the carbon monoxide was found to contain 4.5 to 6 per cent. of carbon dioxide.

Bessemer steel of the following composition was treated:

Constituent	Per cent.
Silicon	0.08
Carbon	0.35
Manganese	0.72
Oxygen	0.28
Magnetic iron oxide	1.02

Ten grammes of this steel when heated to 1000° C. evolved gas as indicated:

[9] *Jour. Iron and Steel Inst.*, 1881, 1, pp. 183–194.

Time of treatment	Cubic centimetres of gas	Per cent. carbon dioxide	Per cent. carbon monoxide	Per cent combustible
First 24 hours	45	2.58	67.74	29.68
Next 24 hours	41	0.66	41.80	57.54
Last 12 hours	5	1.44	8.39	90.07

The specific gravity of the sample being 7.75, one volume of steel evolved 70.5 volumes of gas. This same steel when heated at a low red heat, in an atmosphere of hydrogen, absorbed 6.6 cubic centimetres, or 5.116 volumes of gas; when the temperature was raised, 7.0 cubic centimetres was absorbed, making a total of 10.54 volumes absorbed.

At the time of its publication Parry's work was received with much skepticism. It was very generally believed that a great error was somewhere introduced on account of the large volumes of gas obtained. Parry himself admitted that there was a possibility that his tubes leaked at high temperatures, although he said that he had tested them by blank determinations and had found them to be air-tight. In order that any possibility of a leak at high temperatures might be eliminated, Parry designed a new type of apparatus for his work. This consisted of an evacuated glass tube in which the test specimens could be heated by passing an electric current directly through them. However, the apparatus was evidently not very satisfactory, as no results obtained by its use can be found. In the light of later discoveries by other investigators, it is now conceivable that Parry's tubes did not leak, but that the large volumes of gas actually were evolved from the iron and steel. However, the accuracy of Parry's work is still a matter of doubt.

About 1878, Fr. C. G. Müller[10] conceived the idea that the occluded gases could be liberated from iron and steel by broaching or boring the test specimens under water, in an apparatus constructed on the principle of the accompanying sketch.

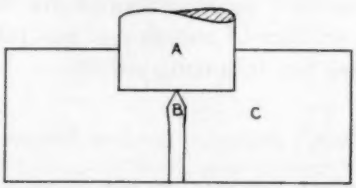
The gas liberated by the bit (*B*) was collected in the hole bored in the metal and could be transferred to a burette for analysis. Samples of iron and steel were bored under water in this way and the gases collected and analyzed. The results were as follows:

[10] *Ber. d. d. Chem. Gesells.*, 1879, **12**, pp. 93–95; 1881, **14**, pp. 6–14. Also, *Stahl u. Eisen*, **4**, 1884, pp. 69–80.

Gas	Sample* (a)	(b)	(c)	(d)
Hydrogen	88.8	77.0	67.8	83.3
Nitrogen	10.5	22.9	30.8	14.2
Carbon monoxide	0.7	.....	2.2	2.5
Gas volume, sample volume	0.6	0.45	0.25	0.35

*(a) Bessemer steel before the addition of spiegel.
(b) Bessemer steel after the addition of spiegel (same charge as (a)).
(c) Martin steel
(d) Wrought iron.

Since such a large percentage of hydrogen was found, Müller thought that perhaps the warm filings were being acted on by the



A. Test Specimen. *B*. Drill. *C*. H_2O tank.

water in which the boring was being done. To prevent such an action, he treated some of the same metals under rape-seed oil and others under mercury. In all cases the results were identical with those obtained when the metals were bored under water. Müller therefore concluded that the gases must have come from the metal.

There were great differences of opinion as to the value of Müller's method of extracting gases. J. E. Stead[11] showed that the volume of gases liberated by a blunt drill was much larger than that obtained by the use of a sharp one, the difference often amounting to one hundred-fold. E. W. Richards[12] decided that the discrepancy was brought about by larger volumes of hydrogen being formed by the decomposition of water when blunt drills were used. To confirm this theory, the cutting edge was removed from a drill and the blunt tool allowed to revolve in contact with a test sample for 24 hours. No hole was bored, yet large quantities of hydrogen were given off. From this Richards concluded that the water had been decomposed. How-

[11] *Jour. Iron and Steel Inst.*, 1882, **2**, pp. 526, 572; 1883, **1**, p. 114. Also, *Iron*, 1883, p. 115; 1884, p. 138.

[12] *Jour. Iron and Steel Inst.*, 1882, pp. 519–520.

ever, Müller's experiments in which the materials were bored under rape-seed oil and mercury are not explained by Richards's theory.

As stated previously, Sir Henry Bessemer[13] had originally observed that molten steel appeared to evolve great quantities of carbon monoxide. When the steel was allowed to cool, violent bubbling occurred and frequently holes known as "blowholes" appeared in the cooled metal. Bessemer noticed that if pressure were placed on the mould in which the steel was cooling, the bubbling ceased, and steel free from "blowholes" was obtained. Bessemer's idea was later incorporated in the Whitworth patent. Müller analyzed a number of samples of gas taken from "blowholes" and obtained the following results:

Müller's Analysis of Gas from Blowholes

Material	Per cent. Ferro-manganese	Per cent. Ferro-silicon	Per cent. Gas evolved	Per cent. CO	Per cent. H	Per cent. N
Soft basic steel. . . .	2.5	...	36.0	0.6	85.4	14.3
Basic steel.	...	...	20.0	...	64.5	35.4
Basic steel.	2.5	5.0	2.2	0.4	86.4	12.7
Basic steel.	...	5.0	6.0	.1.	54.7	45.3

Müller next conducted a comprehensive investigation on the gases evolved during the filling of moulds. A description of the metals and the analyses of the gases collected are given in tabular form as follows:

TABLE II.

Showing Gases Evolved During the Filling of Moulds—Müller.

(Description of material is on pages 176 and 177—see numbers.)

Material. No.	Composition of Material in Per Cent. Comb. C.	Free C	Si	P	Mn	Composition of Gas in Per Cent. CO	H_2	N_2	CO_2	O_2
1	.584	3.104	1.68	.....	1.93	36.1	55.8	3.6	3.7	.8
1a	.....	.....	.....	.....	....	37.3	58.3	.5	3.9	...
2	4.18	.....	.253	.....	7.37	48.1	48.9	2.0	1.2	.4
2a	.....	.....	.....	.....	....	48.7	49.5	.5	1.5	...
3	3.09	.....	.203	3.025	.73	37.1	43.7	14.2	3.3	1.2
3a	.....	.....	.....	.....	....	39.6	46.8	10.0	3.8	...

[13] *Ibid.*, 1881, 1, pp. 197–199.

TABLE II.—*Continued.*

Material No.	Composition of Material in Per Cent. Comb. C	Free C	Si	P	Mn	Composition of Gas in Per Cent. CO	H_2	N_2	CO_2	O_2
4	.23	.....	.15	.06	.5	35.5	45.3	11.3	7.0	1.0
4	.28	.....	.26	.08	.06					
4*a*	.....	.....	.....	.....	....	37.3	47.3	7.9	7.5	...
5						24.1	35.1	29.3	5.9	5.6
5*a*						34.0	49.5	8.6	7.9	...
6	.48	.....	.15	.06	.8	41.7	19.1	37.9	.4	.7
6*a*	.53	.....	.25	.08	.9	43.2	19.7	36.7	.4	...
7						....	....	....	...	...
7*a*						45.9	41.4	9.9	2.8	...
8	Presumably same as No. 4					38.7	51.3	7.2	2.8	...
8*a*	.....	.....	.....	.....	....	43.4	46.9	6.6	3.1	...
9	Presumably same as Nos. 5 to 7					48.2	44.5	2.5	4.8	...
9*a*	.....	.....	.....	.....	....	42.5	36.5	17.1	3.7	...
10	?	?	?	?	?	33.0	47.4	10.0	7.6	2.0
10*a*	.....	.....	.....	.....	....	38.4	51.0	2.2	8.4	...
11	?	?	?	?	?	30.2	37.5	23.8	7.4	.8
11*a*	.....	.....	.....	.....	....	31.5	39.2	21.6	7.7	...
12	?	?	?	?	?	68.6	19.8	9.0	2.0	.8
12*a*	.....	.....	.....	.....	....	70.7	20.7	6.5	2.1	...
13	?	?	?	?	?	15.6	45.4	33.7	1.8	3.2
13*a*	.....	.....	.....	.....	....	18.6	54.2	24.9	2.3	...
14	?	?	?	?	?	17.5	61.1	29.1	2.2	.8
14*a*	.....	.....	.....	.....	....	18.1	52.9	26.8	2.2	...
15	?	?	?	?	?	36.5	26.7	30.5	1.3	4.7
15*a*	.....	.....	.....	.....	....	48.0	35.1	15.4	1.5	...
16	?	?	?	?	?	39.0	36.9	17.8	2.9	3.0
16*a*	.....	.....	.....	.....	....	46.0	43.6	6.9	3.4	...
17–22	.05	.....	Trace	.05	.45	....	....	....	....	...
17–22	.10	.....	Trace	.10	.55	....	....	....	...	...
17–22*a*	....	.....	.....	....	....	65.0	5.0	30.0	...	...
23	.25	.....	Trace	.05	.45	67.2	15.8	12.0	4.7	.3
				.10	.55					
23*a*	.....	.....	.....	.....	....	68.0	16.2	11.0	4.8	...
24	?	?	?	?	?	56.5	33.0	8.6	1.9	...
25	?	?	?	?	?	62.0	34.2	1.0	2.8	...
26	.....	.....	.....	.....	....	77.9	5.7	14.7	1.7	...
26*a*	....	.....	.....	.....	....	62.6	12.6	23.2	1.6	...
27	.....	.....	.....	.....	....	81.7	8.2	9.5	.6	...
27*a*	.....	.....	.....	.....	....	54.1	38.6	3.5	3.8	...
28	.....	.....	.....	.....	....	8.0	71.7	18.0	2.0	...
28*a*	.....	.....	.....	.....	....	8.8	71.9	18.1	2.0	...
29	.....	.....	.....	.....	....	19.3	30.7	41.7	2.1	5.8
29*a*	.....	.....	.....	.....	....	27.3	43.5	26.2	3.0	...
29*b*	.....	.....	.....	.....	....	29.2	32.0	32.0	3.4	3.3
29*c*	.....	.....	.....	.....	....	35.0	38.4	22.5	4.1	...
30	.....	.....	.....	.....	....	58.3	17.0	19.9	1.9	1.8
30*a*	.....	.....	.....	.....	....	64.6	18.9	14.4	2.1	...
30*b*	.....	.....	.....	.....	....	36.2	34.1	22.7	3.0	3.7
30*c*	.....	.....	.....	.....	....	44.1	41.6	10.6	3.7	...
31*a*	.002	.....	.002	.078	.083	....	....	....	...	...
31*b*	.115	.....	.162	.097	.944	....	....	....	...	...
31*c*	.14	.....	.53	.....	1.25	....	....	....	...	...
31*d*	.....	.....	.....	.....	....	34.7	58.0	4.1	3.2	...
31*e*	.....	.....	.....	.....	....	30.8	65.8	1.9	1.5	...

DESCRIPTION OF THE MATERIAL USED IN MÜLLER'S EXPERIMENTS.

A.—Pig Iron.

No. 1. Gray Bessemer pig iron: Copious evolution of gas; block dense, fine grained, and gray, with white crust 1 mm. thick.

No. 1*a*. After calculating the oxygen to air, deducting the corresponding nitrogen, and recalculating to 100.

No. 2. Spiegeleisen: Abundant gas; block dense, flaky, and crystalline.

No. 2*a*. After correction as above.

No. 3. Thomas iron: Less gas than with 1 and 2. Block free from bubbles; radial.

No. 3*a*. Corrected as above.

B.—Bessemer Products.

No. 4. Rail steel: Dense, blown from hot, fused charge with moderate Si and Mn content.

No. 4*a*. Corrected.

No. 5. Spring steel: Dense (cast from above).

No. 5a. Corrected.

No. 6. The same (poured from below).

No. 6*a*. Corrected.

No. 7. The same (without further details).

No. 7*a*. Corrected.

No. 8. Rail steel: Dense, first mould (corrected).

No. 8*a*. After 17 minutes last mould (corrected).

No. 9. Spring steel: Dense, first mould (corrected).

No. 9*a*. After 21 minutes, last mould (corrected).

No. 10. Rail steel: Swelling.

No. 10*a*. Corrected.

No. 11. Rail steel: Swelling more strongly.

No. 11*a*. Corrected.

No. 12. Rail steel: Swelling still more strongly, very restless.

No. 12*a*. Corrected.

No. 13. Bessemer steel: Completely decarbonized and hot-short, before addition of spiegeleisen. Swelling and copious liberation of gas, zone of worm casts, and single bubbles in centre; first gas sample.

No. 13*a*. Corrected.

No. 14. Bessemer steel: Completely decarbonized and hot-short, before addition of spiegeleisen. Swelling and copious liberation of gas, zone of worm casts, and single bubbles in centre; second gas sample.

No. 14*a*. Corrected.

No. 15. Martin steel: Completely decarbonized, as comparison; first gas sample.

No. 15*a*. Corrected.

No. 16. Martin steel: Completely decarbonized, as comparison; second gas sample.

No. 16*a*. Corrected.

C.—Thomas Products.

No. 17 to 22. Thomas metal: Soft, prepared with 95 per cent. ferromanganese; no strong spiegel or ferromanganese reaction; brisk liberation of gas in pots and moulds; poured from below.

No. 17 to *22a*. Mean of corrected analyses.

No. 23 Rail steel: Produced by the addition of 8 per cent. of fused spiegeleisen; strong spiegel reaction.

No. *23a*. Corrected.

No. 24. Rail steel: Produced by the addition of 10 per cent. of spiegeleisen; strong spiegel flame; restless product, rapid swelling; gas from above from fourth block; analysis corrected.

No. 25. Rail steel: Produced by adding 10 per cent. of spiegeleisen; strong spiegel flame; restless product, rapid swelling; gas from above from last block (after nine minutes); analysis corrected.

No. 26. Ingot iron: Gas from below, sampling to be removed directly mould was full.

No. *26a*. Ingot iron: Gas from above by means of sand cover, not filled until mould had set; from same mould.

No. *27*. Rail steel similarly treated; first gas sample.

No. *27a*. Same as No. 27; second gas sample.

No. 28. Ingot iron: Little gas, completely decarbonized, and before the introduction of reducing agents.

No. *28a*. Corrected.

No. 29. Ingot iron: Gassy, completely decarbonized; first gas sample.

No. *29a*. Corrected.

No. *29b*. Second gas sample.

No. *29c*. Corrected.

No. 30. Ingot iron: Prepared with 5 per cent. of 14 per cent. silicide and 2.5 per cent. of 70 per cent. ferromanganese; steel swelling gently, moderately porous (see first table, sample last but one); gas sample from small mould at commencement of pouring.

No. *30a*. Corrected.

No. *30b*. Gas sample from larger mould at end of pouring.

No. *30c*. Corrected.

No. *31a*. Ingot iron: With 5 per cent. of same silicide and 2 per cent. of ferromanganese added red-hot in the pot; no reaction, steel quiet; swelling later with formation of porous zone—before addition.

No. *31b*. After addition.

No. *31c*. (Calculated.)

No. *31d*. Gas from one mould.

No. *31e*. Gas from another mould.

From the data collected during his investigations Müller arrived at the following conclusions: *

" 1. Molten iron and steel contain a mixture of gas consisting of carbon monoxide, hydrogen, nitrogen and carbon dioxide, with

* Von Jüptner: " Siderology," p. 284.

small portions of free oxygen. The mixture is of variable composition, and the gases are present partly in solution and partly in combination (alloyed); hydrogen and nitrogen are alloyed with the iron, and carbon monoxide is present in solution.

"2. As cooling proceeds, there is liberated a mixture of gases, consisting chiefly of carbon monoxide, hydrogen, and nitrogen, the percentage composition fluctuating between certain limits, according to the nature and treatment of the iron.

"3. The solidified metal retains a quantity of imprisoned gas, which may be liberated by broaching. This gas consists mainly of hydrogen and nitrogen, with a small percentage of carbon monoxide.

"4. By heating the metal to redness in a vacuum, small quantities (to be regarded as combined remainders) of the elementary gases can be driven out and determined.

"5. The use of silicon-manganese results in the production of a steel which does not evolve gas during solidification. This phenomenon is probably due to the fact that the silicon-manganese steel becomes supersaturated with gas."

Upon examining the results obtained by Müller in his experiments on broaching under water, it is found that the volume of gas he obtained per unit volume of metal is much smaller than the volumes obtained by Graham and Parry. It seems very probable, therefore, that broaching does not liberate all the gas, and therefore Müller's work does not contribute marked advance over the results obtained by earlier investigators.

A. Pourcel[14] conducted a number of experiments dealing with the effects produced on steel by the addition of silicon and manganese. He found that castings free from blowholes could be produced by the addition of alloys of silicon, manganese, and iron, with a minimum of carbon. If ferromanganese was added to a bath of molten metal, a violent reaction occurred, accompanied by the evolution of carbon monoxide. The resulting castings contained large numbers of blowholes. If silicide of manganese was added, no bubbling of gas was evident, and castings free from blowholes were produced, although flames of hydrogen were visible at the point of solidification. If silicon was added as silicide of iron, hydrogen could not be thus detected,

[14] *Jour. Iron and Steel Inst.*, 1882, pp. 509–518.

and no blowholes were formed. From the above results it was concluded that silicon steel contained almost no gas unless manganese was present. The gas was found to increase with the percentage of manganese until, with 2 per cent. of manganese, the largest amount of gas with a maximum content of hydrogen was found to be present. Aluminum produced the same effect as silicon.

Pourcel disagreed with Müller as to the manner in which the carbon monoxide was occluded. Pourcel assumed that the carbon monoxide was formed by the action of oxygen on the carbon in the steel. The affinity of silicon and aluminum for oxygen being greater than the affinity of carbon for oxygen, when the two first-named elements were present, they acted as reducing agents and no gas was formed. Pourcel's theory became known as the "reaction theory," whereas Müller's theory that the carbon monoxide was in solution in the steel was called the "solution theory."

Considerable information as to the nature of the gases occluded in weld and ingot iron is given in the results of a series of investigations by Zyromski,[15] in which he extracted the gas from the metal under examination by means of an apparatus resembling that used by Graham. Identical portions of pig iron were converted into puddled and ingot iron, respectively, and the gases extracted from the finished products analyzed. The following table shows the analyses of the gases evolved from four test bars of ingot and four of puddled iron:

Determination	Material	Weight of bar in grammes	Volume of gas per cubic centimetre of sample	Percentage composition		
				H	CO	N
1	Ingot iron.....	24.242	16.00	58.4	5.6	36.0
2	Ingot iron.....	23.650	18.55	60.9	5.9	33.2
3	Ingot iron.....	24.450	16.95	52.5	13.5	33.9
4	Ingot iron.....	24.432	16.80	56.8	6.8	36.4
5	Puddled iron.....	24.353	16.15	27.8	40.3	31.8
6	Puddled iron.....	23.995	14.10	15.6	45.3	39.0
7	Puddled iron	24.851	16.55	30.8	45.4	23.8
8	Puddled iron.....	23.453	15.25	22.3	45.5	32.1

[15] *Compt. rend. de la Société de l'Industrie Minerale*, 1884, pp. 101–108.

The composition of the metal tested was stated to be as follows:

Element	Ingot iron	Puddled iron
Carbon	0.050 per cent.	0.030 per cent.
Silicon	Trace	
Sulphur	Trace	
Phosphorus	0.024 per cent.	0.078 per cent.
Manganese	0.288 per cent.	0.200 per cent.

The results of the gas analyses show that, while the volumes of the gases contained in the two products were approximately the same, the puddled iron contained about five times as much carbon monoxide as the ingot iron, but considerably less hydrogen.

In his "Metallurgy of Steel" (pp. 105–145), published in 1892, Henry Howe gave an excellent *résumé* of the results obtained to that date concerning the subject of occluded gases. Howe considered that occluded gases might be divided into four separate and distinct classes: (1) Those chemically combined; (2) those in solution; (3) those in adhesion; (4) those mechanically retained in the pores of the metal. Of these four states, the first three are non-gaseous and the fourth alone is gaseous. Howe discussed the relationship between iron and nitrogen, iron and hydrogen, and iron and carbon monoxide, laying particular emphasis on the effects which these gases produce on the physical properties of the metal. His discussion may be summarized as follows:

Iron and Nitrogen.—Iron changes in appearance on being heated in a stream of ammonia, the metal becoming brittle and acquiring a bright fracture. The change is due to the absorption of nitrogen, hydrogen being set free.

Nitrogen imparts a relatively low ductility to steel.

Nascent iron absorbs nitrogen from the atmosphere, the nascent iron being formed by the reduction of iron oxide by carbon.

Ammonia, as such, can be occluded by iron, a distinct odor of ammonia having been detected upon fracturing castings.

Iron and Hydrogen.—Molecular hydrogen appears to have little effect on iron. In one case, after occluding 46 volumes of hydrogen, iron was found to have acquired a slightly white color; and, in another case, after being heated for some hours in hydrogen, the iron was found to have become slightly brittle, crystalline, and of a steel-like appearance.

Nascent hydrogen causes iron to become brittle, affects the elongation of iron anomalously, causes the flexure of iron to fall, and decreases the cross-sectional strength of steel springs from 14.6 to 47.6 per cent.

Contact with zinc intensifies the above effects, and heating or resting restores the iron to its original condition.

Iron and Carbon Monoxide.—There is but little evidence that carbon monoxide influences the properties of iron. Possibly it acts slightly like phosphorus and makes iron cold short. It is suggested that, since Whitworth's liquid compression increases the quantity of gas dissolved, and since the steel manufactured by Whitworth's method is of very good quality, carbon monoxide cannot exert a harmful influence on the steel.

Howe's conclusions as to the manner in which the above gases are inclosed in iron and steel are given in his own words, as follows:

"To sum this discussion up, very numerous analyses of the gases which iron evolves, before, during, and after solidification, on boring and on heating *in vacuo*, prove that these gases usually consist chiefly of hydrogen and nitrogen which, according to the definitions made in order to render discussion of the points at issue possible, must escape from solution.

"But, wholly independently of this conclusive evidence, the behavior of gases toward iron, their absorption and release from both solid and molten metal on rise and fall of pressure, their expulsion on solidification and agitation, their protracted escape, and the shape and position of the cavities which they form, is closely analogous to their behavior towards other solvents. The closeness of this analogy; our inability to reconcile the copious escape of gas from iron low in silicon with the complete arrest of the escape of gas by slight additions of this element on the 'reaction theory,' and the complete accord of these phenomena with the 'solution theory'; the fact that gases are copiously evolved from both oxygenless and nearly carbonless iron and from other classes in which no gas-forming reaction is to be looked for; and that their escape cannot be accounted for qualitatively or quantitatively by purely mechanical retention of insoluble gas, all point with varying degrees of certainty and, taken collectively, lead irresistibly to the conclusion that gases dissolve in iron, and that

at least a very large part of these gases, whose escape forms blowholes, are dissolved in the metal before that escape.

"If successful, the attempt to show that the hydrogen and nitrogen alone found in boring cold iron proceed from the water in which it is bored, and not from the iron, would not seriously bear against the remaining evidence and reasoning. But the ratio of nitrogen to hydrogen in these gases and their freedom from oxygen; the fact that the gases obtained in the two instances in which iron has been bored under oil and mercury resembled in composition those obtained on boring under water; the fact that compact yields less gas than porous iron, and the arrangement of the boring apparatus, collectively argue cogently against the aqueous source of the gases. That the absence of carbonic oxide from these gases is not due to its conversion into carbonic acid and subsequent absorption by the boring water is indicated by the facts that this conversion could not be complete, that neither carbonic oxide nor acid is found on boring under oil and mercury, and that in case of blisters both these gases are found even on boring under water.

"Further, the changes in the composition of the gases evolved from iron, so far as we have studied them, are quite compatible with the view that they are evolved from solution.

"Turning now to carbonic oxide, which accompanies hydrogen and nitrogen in all except the boring gases, there is reason to believe that, in spite of its absence from the blowholes when the metal is cold, it coöperates in forming them while the metal is hot, and is later reabsorbed or decomposed. (1) The general similarity of its behavior to that of hydrogen and nitrogen; (2) its expulsion and absorption under falling and rising pressure; (3) its escape, occurring when no reaction is to be expected, and arrested by silicon when this element appears to act on the solubility and not by being preferentially oxidized; these three collectively very strongly indicate that carbon oxide dissolves, and it may reasonably be held that they do not prove it. Were carbonic oxide known to dissolve, then in coöperating with hydrogen and nitrogen in the formation of blowholes it would be most natural to suppose that, in the majority of cases, it escaped from solution like its companions.

In a word, it is practically certain that in the many and important classes of cases which have been studied the blowhole-

forming gases are chiefly hydrogen and nitrogen escaping from solution; it is extremely probable that carbonic oxide coöperates, and that it, too, comes in large part from solution. Under other and yet unstudied conditions air mechanically drawn down in teeming may, however, prove to be an important cause of blow-holes."

During 1903–1906 Hjalmar Braune[16] discovered that iron manufactured in certain Swedish blast furnaces was brittle and non-elastic. He ascribed these properties to the high nitrogen content of the iron, it having been known since 1860[17] that a high nitrogen content tends to make iron brittle. During his researches Braune decided that the nitrogen was present in the iron in two forms—nitrogen held mechanically and nitrogen held chemically—and that the brittleness of certain grades of iron was due to the chemically combined nitrogen. He accepted the experiments of Müller and of Stead as typifying the liberation of mechanically held nitrogen, and then conducted some investigations with the object of discovering the form in which the chemically combined nitrogen was present. In order that cyanides might be tested for, some of the Swedish iron was dissolved in hydrochloric acid, and the gas evolved was tested for hydrocyanic acid. None was present, and Braune therefore concluded that the nitrogen was not present as a cyanide. Another sample of the same iron was dissolved in hydrochloric acid and tests for ammonia made. Large quantities of ammonia were dissolved. A sample of iron nitride was treated with hydrochloric acid and the same result was obtained, and it was therefore concluded that the nitrogen was present as iron nitride, having the probable formula Fe_5N_2.

Braune likewise discovered that the presence of nitrogen in iron could be detected by means of photomicrographs. Iron free from nitrogen appeared to be composed of large cells having a uniform surface, and to be marked by a number of parallel striations of corrosion. Some cells seemed to have disappeared altogether, and a crystalline structure developed in their place. With a nitrogen content of 0.07 per cent. to 0.08 per cent. the cells were about one-tenth of their original size; with a nitrogen con-

[16] *Stahl u. Eisen*, **26**, 1906, pp. 1357–1363, and *Revue de Metall.*, 1905, pp. 497–502; *Ibid.*, 1907, p. 834.

[17] Fremy, *Compt. rend.*, **52**, 1861, p. 323.

tent of 0.02 per cent. the cells had entirely disappeared, the resulting crystalline structure very closely resembling that of pearlite.

Nitrogen was found to affect the temper and also to augment the coercitive force and the hysteresis effect of steel.

As has been stated previously, the presence of blowholes had been recognized for a number of years, and many investigators had sought to discover some means by which these imperfections could be avoided. In 1907 W. Kusl[18] endeavored to show that carbon monoxide was the chief cause of blowholes. Kusl considered that the greater part of the hydrogen and nitrogen originally present was evolved before the metal solidified, and, in proof of his theory, analyzed the gases obtained from a number of blowholes. It was found that carbon monoxide was present in large percentages, with smaller amounts of hydrogen and nitrogen, as the following table indicates:

Gas	Per cent.
Carbon monoxide	52.00
Hydrogen	27.46
Carbon dioxide	7.40
Nitrogen	13.20
Total	100.06

Kusl concluded that sound castings could be best obtained by dealing as far as possible with the carbon monoxide, the source of the reaction blowholes; by using warm and well-dried moulds; and by rapid after-pouring. He concluded further, however, that there was at that time no practical method of entirely avoiding the formation of blowholes.

E. von Maltitz[19] conducted a number of investigations on the problem of discovering whether or not molten steel absorbed gas. He concluded that heating to very high temperatures seemed to diminish any tendency to this action, should any exist, since steel poured extremely hot (and without over-oxidation) yielded perfectly solid ingots and castings. Analyses of the gases obtained from a number of blowholes were made, and it was found that the gases varied widely in composition and always contained

[18] *Osterreichische Zeitschrift für Berg. und Hüttenwesen*, 54, pp. 593–598; 610–613.

[19] *Bi-monthly Bull. Am. Inst. Min. Eng.*, 1907, pp. 691–726.

far higher proportions of hydrogen than of nitrogen. This may be seen from the following table, giving the results of Maltitz's analyses:

Gas	Per cent.
Hydrogen	54.7 to 92.4
Nitrogen	5.9 to 45.3
Carbon monoxide	0.0 to 2.2

Von Maltitz was unable to determine the form in which the hydrogen was present, but stated that it seemed to be alloyed with the metal.

Analyses of gases from cooling ingots showed a composition differing considerably from that of the gases obtained from blowholes:

Gas	Per cent.
Hydrogen	16.2 to 54.2
Nitrogen	2.2 to 36.7
Carbon monoxide	18.1 to 68.0
Carbon dioxide	Small amounts

From the above results von Maltitz arrived at the following conclusions:

1. Although practically only hydrogen and nitrogen are found in blowholes, these two gases are not entirely responsible for blowholes.

2. An important factor is carbon monoxide, which is present in large quantities in solidifying steel.

3. The source of the carbon monoxide is the ferrous oxide dissolved by the steel during its manufacture.

4. The solvent power of steel for ferrous oxide increases with the temperature.

5. Steel also dissolves ferrous oxide in proportion to the purity of the steel.

6. The affinity of iron for oxygen at high temperatures increases more rapidly than the affinity of carbon for oxygen.

Von Maltitz next considered the physical conditions attending the formation of blowholes, and suggested methods for their complete elimination. These methods included the prevention of over-oxidation, the reduction of the oxidized material, and a choice between "heat finishing" in the furnace. The influence of the presence of carbon manganese, silicon, and aluminum in preventing blowholes was also considered. Incidentally it was

observed that pig iron did not form blowholes on freezing. It was concluded that the absence of blowholes was due to the fact that pig iron possesses a very low solvent power for ferrous oxide and also to the fact that there was no pasty state intermediate between the molten and solid states. Reference was made to the effect of stirring the steel in the ladle, the variation in the methods of pouring, and the influence exerted by increased and decreased pressure. The following precautions are suggested in order to prevent the formation of blowholes:

"1. During the last period of the process, in the converter or open-hearth furnace, the melt should be held at a medium temperature.

"2. Excessive additions of ore and 'over-blowing' should be avoided.

"3. The finishing slag should not be too rich in oxygen and should have a proper degree of fluidity.

"4. Ferrous oxide should be decomposed by stirring the heat before tapping. There should be added sufficient oxidizing materials for the separating of manganese protoxide, and the silicate of manganese or aluminum formed in the slag."

Two Frenchmen, G. Belloc and O. Boudouard, working independently, have made many contributions to the knowledge of occluded gases.

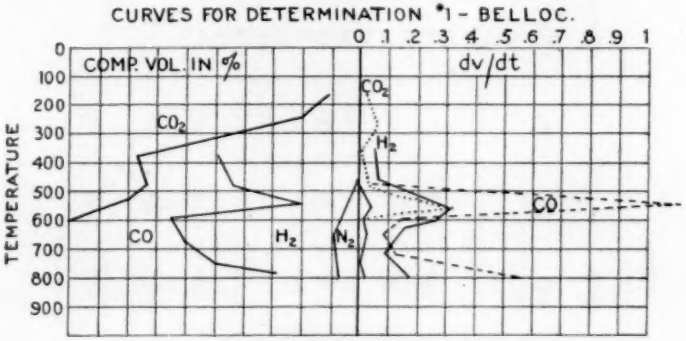
In his earlier work Belloc[20] sought to establish some relationship between the temperature (t) of the iron, the rate of evolution (dv/dt) of the gas, and the composition of the gas. He used an externally glazed porcelain tube about 60 cm. long and heated it electrically. The method of heating is not described in detail. Temperatures were measured with a Le Chatelier pyrometer. The steel used was of the following composition:

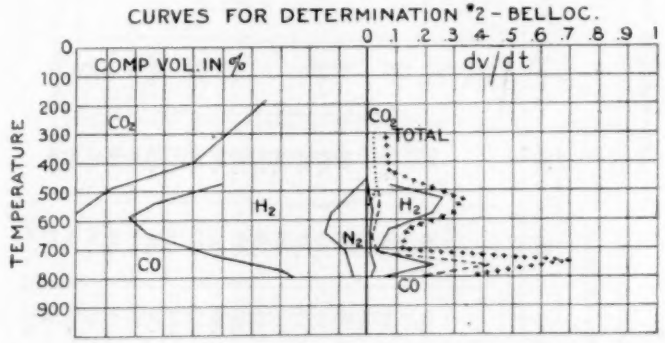
Element	Percentage
Carbon	0.12
Silicon	0.03
Sulphur	0.02
Phosphorus	0.018
Manganese	0.36

[20] *Compt. rend.*, **145**, 1907, pp. 1280–1283; *Revue de Metall.*, **5**, 1908, pp. 469–488.

Some of the results which Belloc obtained by heating the steel to 1000° to 1100° C. for several days at a time are shown in Table III on page 28.

From Belloc's figures it is seen that the evolution of gas began at 150° to 400° C. (dv/dt), had a minimum value at 200° C. and a maximum at 400° C. Between 500° and 600° C. there was a high maximum, falling off to a minimum at 600° C.





Upon heating the metal above 600° C., the evolution of gas increased. At 1200° C. the volume of gas obtained was eleven or twelve times the volume of the steel. The gas evolved up to 400° C. was mostly carbon monoxide, which was not present in the sample taken at 550° C. Above 400° C. hydrogen was evolved, and the gas given off above that temperature consisted almost completely of hydrogen, although above 550° C. a quantity of nitrogen, not exceeding 10 per cent., appeared.

TABLE III.

Determination Number 1.—*Belloc.*

Temperature	Vol. (v), extracted in c.c.					dv/dt					Composition per cent. in volumes			
t	Total	CO_2	CO	H_2	N_2	Total	CO_2	CO	H_2	N_2	CO_2	CO	H_2	N_2
150	.26	.24									90			
190	.10	.09				.03	.02				90			
250	.40	.35				.07	.06				80			
280	.35	.25				.12	.08				70			
390	.80	.20	.20	.40		.07	.02	.02	.04		25	25	50	
480	1.15	.32	.32	.51		.13	.04	.04	.06		28	28	44	
540 *a*	2.60	.50	1.75	.35							34	52	14	
b	1.50	.36	.80	.34							34	54	22	
c	1.95	.70	1.05	.15	.05						36	54	8	2
d	.90	.10	.53	.24	.03	1.84	.37	1.11	.33	.03	11	60	27	2
e	1.70	.10	1.10	.47	.03						6	65	28	1
f	1.85	.35	1.10	.36	.04						19	60	20	1
g	.60	.10	.37	.08	.05						16	62	13	9
600 *a*	1.41	.02	.33	.01	.05	.42		.14	.26	.02	2	23	72	3
b	1.10	.01	.50	.53	.06						1	45	48	6
660 *a*	1.10		.49	.52	.09	.27		.10	.14	.03		45	47	8
b	.51		.14	.31	.06							27	61	12
730 *a*	1.00		.52	.44	.04	.23		.12	.10	.01		52	44	4
b	.63		.33	.28	.02							..	..	..
800 *a*	1.55		1.10	.39	.06							71	25	4
b	1.90		1.48	.36	.06	.79		.57	.19	.03		78	20	2
c	1.35		.97	.32	.06									
d	.72		.41	.25	.06							57	35	8
	25.43	=4 times vol. of steel.												

50 G. of steel used.

TABLE III.

Determination Number 2.—Belloc.

Temperature	Volume (v), extracted in c.c.					dv/dt					Composition, per cent. in volumes			
t	Total	CO_2	CO	H_2	N_2	Total	CO_2	CO	H_2	N_2	CO_2	CO	H_2	N_2
200	.15	.10									65			
310	.30	.15				.03	.01				50			
390	.20	.08				.03	.01				40			
480	1.05	.16	.27	.62	N_2	.13	.02	.03	.08		15	26	59	
520	1.42	.10	.17	1.08	.07	.35	.03	.04	.27	.02	7	12	76	5
580 *a*	1.25		.13	.96	.16	.30		.03	.24	.04		10	77	13
b	.58		.03	.48	.07							5	83	12
630	.60		.08	.43	.09	.12		.02	.09	.02		13	72	15
710	.80		.28	.45	.07	.10		.04	.06	.01		35	56	9
760 *a*	1.52		.84	.60	.08							55	40	5
b	1.20		.75	.41	.04	.71		.42	.26	.03		63	34	3
c	.83		.50	.30	.03							60	36	4
800	1.19		.79	.34	.06	.30		.20	.09	.02		66	29	5
	11.09	=1.15 times vol. of steel.												

75 G. of steel used.

TABLE IV.

Gases Occluded in a Special Nickel Steel—Belloc's Work.

DETERMINATION NO. 1—50 GRAMMES OF FILINGS.

Temperature, t	Volume (v) Cubic centimetre	dv/dt	Composition per cent. of the gas in volume CO_2	CO	H_2	N_2
480	5.60	0.3	34	51	15	0
540	2.05	.3	1	58	35	6
690	3.20	.2	0	69	27	4
820	4.20	.32	0	76	16.6	7.4
960 a.	5.30	.4	0	75	11	14

Total volume .....21.15—3.5 times the volume of the metal.

DETERMINATION NO. 2—50 GRAMMES OF WIRE.

Temperature, t	Volume (v) c.c.	dv/dt	Composition per cent. of the gas in volume CO_2	CO	H_2	N_2
350	0.95	....	37	40	23	0
440	1.36	0.15	14	26	60	0
540	3.00	.30	12	17	63	8
610	3.70	.53	8	49	39	4
640 a.	8.30	3.50	0	57	37	6
640 b.	2.14	....	0	50	44	6
710	7.70	1.10	0	57.8	40	3.2
740	2.70	.90	0	49	47	4
760	4.00	2.00	0	49	47	4
820	2.35		0	56	40.8	3.2
830 a.	12.50	2.40	0	57	40.8	2.2
830 b.	2.35		0	57	40.8	2.2
950	11.20	.93	0	67	28.5	4.5

Total volume ....61.97—10 times the volume of the metal

Belloc[21] also experimented with a special nickel steel containing 45 per cent. nickel and 0.15 per cent. carbon. Table IV shows the gases obtained from this material. It will be observed that the gases found consisted of carbon dioxide, carbon monoxide, nitrogen, and hydrogen. It was found that carbon dioxide was completely evolved at 520° C., but that, at that temperature, the nitrogen had just begun to appear. Part of the material used was in the form of wire and part in the form of filings. A comparison between the results obtained with these two forms is very interesting. From the filings a total gas volume equal to three and one-half times the volume of the alloy used was obtained. A curve between (t) and (dv/dt) was obtained

[21] *Revue de Metall.*, **5**, 1908, pp. 571–574.

which was nearly parallel to the temperature axis. The yield of carbon monoxide equalled 75 per cent. The rate of evolution of hydrogen reached its maximum at 540° C., and then gradually decreased. The volume of gas obtained from the wire was ten times the volume of the alloy used. The curve (dv/dt) showed two very sharply prominent maxima at 540° C. and 930° C. At 540° C. a minimum of carbon monoxide and a maximum of hydrogen were observed. Above 540° C. the amount of carbon monoxide increased, but very irregularly. The difference between the absolute gas volumes obtained at the same temperatures from filings and from wires can be attributed to:

1. A very unequal distribution of gas in the block. Such a condition has been found to be the case in carbon steels.

2. A large loss in mechanically enclosed gas by the mechanical action of the drills.

3. An absorption of gas during the necessary operations of wire-drawing.

Boudouard[22] carried out a number of determinations by heating samples in an apparatus consisting of: a glazed porcelain tube, about 40 cm. long and 1.9 cm. in external diameter, enclosed in a similar tube, about 46 cm. long and 3.6 cm. in external diameter. By means of this arrangement it was hoped to decrease the possibility of leakage at high temperatures.

The grades of iron used in the determinations were: (1) commercial iron in the form of a bar one square cm. in cross-section (0.099 per cent. carbon); thin plates, 1 mm. thick (0.13 per cent. carbon); 2 mm. thick (0.188 per cent. carbon); 1 mm. thick (0.074 per cent. carbon); and ½ mm. thick strong wire (0.047 per cent. carbon). In the first experiments the materials were slowly heated to the desired temperature, 900° to 1100° C., for a period of one-half hour. The temperature was then held constant at its maximum for one hour, and the tube kept evacuated during the cooling process. The gas evolved was collected and analyzed. Two determinations were made at 445° C. For the first determination, the material was in the form of wire; for the second, filings were used. The first determination yielded a negative result, but in the second case 6.45 c.c. of gas especially rich in hydrogen and carbon monoxide was evolved. Thus it

[22] *Compt. rend.*, **145**, 1907, pp. 1283–1284; *Revue de Metall.*, 1908, **5**, pp. 69–74; *Bull. Soc. Chim.*, 1908, 3, pp. 247–254; 1908, 5, pp. 69–74.

would appear that the physical condition of the metal influenced the development of the gas. It was determined, however, that, in all cases, using wire, bar, or filings, evolution of the gases commenced at red heat.

The composition of the gas evolved at the higher temperatures was studied in two series of analyses, and between each series of two consecutive heatings the material was permitted to lie exposed to the air. As may be seen from Table V, it was exceedingly difficult to remove all of the gas. Even after the third heating gas was evolved, the volume of which depended very largely on the size of the particles of the metal used. Since it was observed that the volume of gas evolved diminished with each heating, it was concluded that a single heating at a temperature sufficiently above 1100° C. to melt the material should evolve all the occluded gas. With the apparatus used, however, it was impossible to obtain such a temperature, as the porcelain tubes leaked above 1100° C. As noted in Table V, the gas evolved consisted mostly of hydrogen and carbon monoxide. At high temperatures the amount of carbon dioxide diminished and that of hydrogen and of carbon monoxide increased. Boudouard concluded that the carbon in the gases formed was due to the combustion of the carbon in the metal (Table V), and also that the volume of gas evolved was proportional to the masses of sulphur and phosphorus in the iron and steel being investigated. Another interesting fact brought to light at this time was that the iron used commenced to volatilize at 900° C., and that this volatilization became very noticeable at 1100° C.

In 1909, E. Goutal[23] published a description of a newly discovered method for the determination of occluded gases. The metal on which he conducted his experiments was dissolved in a slightly acid solution of the double chloride of copper and potassium at a temperature of 40° C. A gas containing a small proportion of carbon monoxide equal in volume to from one-third to four-fifths the volume of the steel used was evolved. It should be noted, however, that Goutal's investigations could not be very exhaustive, since the results for hydrogen obtained were necessarily nullified by the fact that the solution used was acidic.

[23] *Seventh Inter. Cong. Appl. Chem.*, 1909; also, *Metallurgie*, 7, 1910, p. 340.

TABLE V.

Number 1; Series Number 1.—Boudouard.

Nature of metal	Mass G.	Vol. c.c.	Surface sq. cm.	1. Heating to 900° C.		2. Heating to 900° C.			1. Heating to 1100° C.			2. Heating to 1100° C.		
				Vol. of gas, c.c.	Vol. of gas / vol. of metal	After days	Vol. of gas, c.c.	Vol. of gas / Vol. of metal	After days	Vol. of gas, c.c.	Vol. of gas / Vol. of metal	After days	Vol. of gas, c.c.	Vol. of gas / vol. of metal
Wire of .5 mm.	4.25	.545	33	5.8	10.6	60	1.8	3.3						
Wire of 1 mm.	5.0	.641	33	4.0	6.2		1.85	2.8	30	6.2	2.2	19	6.7	2.4
Wire of 2 mm.	12.0	1.538	33	6.15	4.0		4.15	2.7						
Wire of .5 mm.	39.5	5.1	308	45.0	8.8				32	9	1.8	14	4.06	.8
Wire of 1 mm.	31.0	4.0	165	26.1	6.5				32	4.05	1.0	16	2.25	.56
Wire of 2 mm.	61.0	7.692	163	51.0	6.6				36	15.5	2.0	19	8.6	1.1
Bar of 1 cm.	38.7	5.0	22	7.1	1.4				33	3.5	.7	22	2.85	.57
Plate of 1 mm.	56.5	7.25	120	27.0	3.7				33	16.0	2.2	22	10.65	1.5

Number 2; Series Number 2.—Boudouard.

Nature of metal	Mass G.	Vol. c.c.	Surface sq. cm.	1. Heating to 1100° C.		2. Heating to 1100° C.			3. Heating to 1100° C.		
				Vol. of gas, c.c.	Vol. of gas / Vol. of metal	After days	Vol. of gas, c.c.	Vol. of gas / Vol. of metal	After days	Vol. of gas, c.c.	Vol. of gas / Vol. of metal
Wire of .5 mm.....	34	4.36	280.5	24.75	5.7	17	5.8	1.3	13	3.15	.72
Wire of 1 mm.....	40	5.12	213.3	29.5	5.7	18	4.2	.82	15	2.75	.53
Wire of 2 mm.....	40.5	5.2	108.8	25.5	4.9	22	10.4	2.0	19	7.15	1.3
Bar of 1 cm. (1).....	38.6	5.0	22.0	4.15	.8	24	5.4	.54	21	5.15	.51
Bar of 1 cm. (2).....	38.7	5.0	22.0	2.8	.56						
Plate of 1 mm. (1)....	41.0	5.25	80	25.25	4.8	23	15.3	1.4	23	9.7	.91
Plate of 1 mm. (2)....	41.5	5.32	80	38.50	5.3						
Filings of 1 cm. bar...	46.0	5.9	very large	85.0	16.1	17	21.0	3.56	4	.5	.08

TABLE V.

No. 3.—Gas Analysis of First Series—Boudouard.

Nature of metal	Nature of determination	Vol. of gas, c.c.	Vol. of gas / Vol. of metal	CO_2	H_2	CO	N_2	Per cent. composition			
								CO_2	H_2	CO	N_2
Wire of .5–1 and 2 mm.	1. Heating to 300° twice, then 1100°	6.2	2.2	.52	2.0	3.5	.18	8.05	32.26	56.45	3.23
	2. Heating to 1100°	6.7	2.4	.12	2.66	2.84	1.08	1.8	39.7	42.4	16.1
Wire of .5 mm.	1. Heating to 300° once, then 1100°	9.0	1.8	1.58	3.67	3.53	.22	17.5	40.8	38.2	3.5
	2. Heating to 1100°	4.06	.8	.46	1.34	1.18	1.08	11.3	33.0	29.1	26.6
Wire of 1 mm.	1. Heating to 300° once, then 1100°	4.05	1.0	.51	1.85	1.62	.07	12.6	45.6	40.0	1.8
	2. Heating to 1100°	2.25	.56	.37	.94	.41	.53	16.4	41.8	18.2	23.6
Wire of 2 mm.	1. Heating to 300° once, then 1100°	15.5	2.0	2.6	2.62	10.28	.53	16.8	16.9	66.3	23.6
	2. Heating to 1100°	8.6	1.1	.66	2.66	4.91	.37	7.7	30.9	57.1	4.3
Bar of 1 cm...	1. Heating to 300° once, then 1100°	3.5	.7	.10	.82	2.28	.30	2.86	23.42	65.15	8.57
	2. Heating to 1100°	2.85	.57	.15	.72	1.57	.29	5.2	25.6	55.1	14.1
Plate of 1 mm.	1. Heating to 300° once, then 1100°	16.0	2.2	1.51	2.05	12.4	.04	9.4	12.8	77.5	.3
	2. Heating to 1100°	10.65	1.5	.51	3.16	6.72	.26	4.7	23.7	63.1	.25

TABLE V.

No. 4.—Gas Analysis of Second Series.—Boudouard.

Nature of metal	Nature of determination	Vol. of gas, c.c.	Vol. of gas / Vol. of metal	CO_2	H_2	CO	N_2	Per cent. composition			
								CO_2	H_2	CO	N_2
Wire of .5 mm.	1. Heating to 1100° C.	24.75	5.7	5.47	7.57	10.95	0.76	22.1	30.6	44.2	3.1
	2. Heating to 1100° C.	5.8	1.3	.48	2.64	1.02	1.66	8.3	45.5	17.6	28.6
	3. Heating to 1100° C.	3.15	.72	.27	1.68	.73	.47	8.5	53.1	23.1	15.3
Wire of 1 mm.	1. Heating to 1100° C.	29.5	5.7	6.54	4.43	18.03	.50	22.17	15.01	61.12	1.7
	2. Heating to 1100° C.	4.2	.82	.24	1.85	1.71	.60	5.7	39.3	40.7	14.3
	3. Heating to 1100° C.	2.73	.53	.23	1.75	.49	.26	8.4	64.1	17.9	9.6
Wire of 2 mm.	1. Heating to 1100° C.	25.5	4.9	3.68	5.72	15.88	.22	14.4	22.4	62.3	.9
	2. Heating to 1100° C.	10.4	2.0								
	3. Heating to 1100° C.	7.15	1.3	.26	2.37	4.26	.26	3.65	33.1	59.6	3.65
Bar of 1 cm.	1. Heating to 1100° C.	2.8	.56	.26	1.06	1.7	.04	3.65	37.8	60.7	1.5
	2. Heating to 1100° C.	5.4	.54	.2	1.78	3.42	.04	3.8	32.9	63.3	1.5
	3. Heating to 1100° C.	5.15	.51	.31	1.49	3.16	.19	6.0	28.9	61.3	3.8
Plate of 1 mm.	1. Heating to 1100° C.	28.5	5.3	3.61	5.74	18.79	.36	12.7	20.1	65.9	1.3
	2. Heating to 1100° C.	15.3	1.4	.81	4.34	9.85	.30	5.3	28.3	64.4	2.0
	3. Heating to 1100° C.	9.7	.91	.66	2.62	5.97	.45	6.8	27.0	61.6	4.6
Filings of 1 cm. Bar	1. Heating to 1100° C.	85	16.1	4.4	21.7	54.5	4.4	5.2	25.5	64.1	5.2
	2. Heating to 1100° C.	21	3.50	.76	7.47	11.95	.82	3.6	35.6	57.0	3.8
	3. Heating to 1100° C.	.5	.08				.82				

No. 5.—C. Contents—Boudouard.

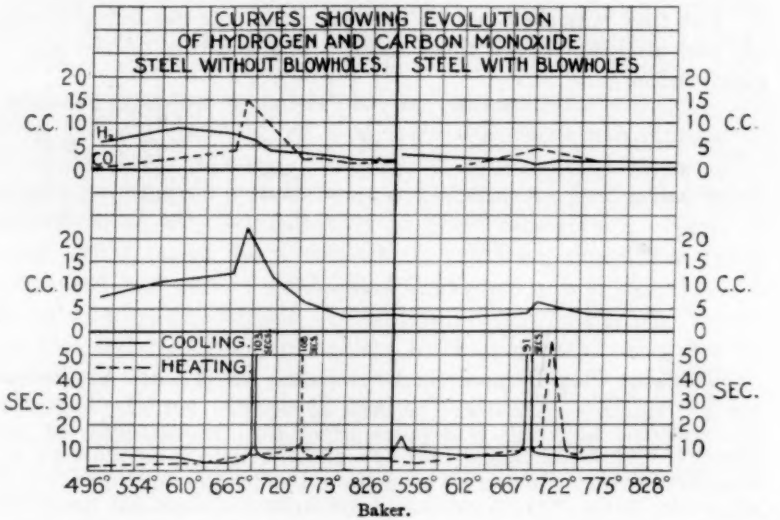
Nature of metal	Mass G.	C-start, G.	C-finish, G.	C-loss, G.	C. in gas, G.
Wire of .5 mm	34	0.016	0.0060	0.01	0.0101
Wire of 1.0 mm	40	.0296	.0132	.0164	.0185
Plate of 1.0 mm	82.5	.1075	.0767	.0308	.0315
Filings	46	.0450	.0230	.0220	.0384

No. 6.—Boudouard.

Nature of metal	Nature of determination	Mass G.	Vol. of gas, c.c.	Volume in c.c.				Weight in G.				Gas per cent. of metal				
				CO_2	H_2	CO	N_2	CO_2	H_2	CO	N_2	CO_2	H_2	CO	N_2	Sum
Wire of .5 mm.	Heat to 1100° C.	34	33.7	6.22	11.89	12.7	2.89	.012	.0011	.016	.0036	.035	.0032	.047	.0105	.0957
Wire of .5 mm.	Heat to 1100° C.	50	36.43	7.01	7.83	20.23	1.36	.014	.0005	.025	.0017	.035	.0017	.062	.004	.1029
Wire of .5 mm.	Heat to 1100° C.	82.5	78.75	5.08	17.4	53.46	2.81	.01	.0017	.067	.0035	.012	.0018	.081	.0042	.099
Filings	Heat to 1100° C.	46	106	5.16	29.17	66.45	5.22	.01	.0026	.083	.0065	.021	.0056	.018	.0142	.02207

At the meeting[24] at which Goutal made public the above results Andrew C. J. Charlier read a report of some experiments he had conducted on the solubility of hydrogen in iron and steel. He asserted that ordinarily iron and steel would absorb hydrogen up to 25 volumes, but that, in the case of electrolytic iron, the proportion was increased to 100 volumes.

Thomas Baker[25] conducted a number of investigations on occluded gases with the following three-fold purpose: To ascertain the nature and volume of the gas evolved when steel was heated in a vacuum; to find the relation, if any existed, between



Baker.

the critical points of steel and the extent of evolution of gas; and to determine the part played by these gases in the production of blowholes.

Baker used porcelain tubes very similar to those employed by Belloc and Boudouard. In connection with the use of these tubes, he made the observation that it was very difficult to obtain tubes which were impervious to gases above 900° C., as many as six often being tested before an air-tight one was secured. Before using his apparatus Baker made a number of blank determina-

[24] *Seventh Inter. Cong. Appl. Chem.*, London, 1909.

[25] *Jour. of Iron and Steel Inst.*, Carn. Schol. Mem., 1909, 1, pp. 219–229; *Ibid.*, 1911, 3, pp. 249–259.

tions in order to determine whether or not any error would be introduced by the apparatus. When the tube was heated under a vacuum for three days, 1.29 c.c. of gas of the following composition was evolved:

Gas	Percentage
Hydrogen	52.7
Carbon monoxide	7.8
Methane	20.9
Nitrogen	18.6
Total	100.00

The tube was then heated for nine days, the gas being drawn off and analyzed every three days. The analysis of the gas is given below:

	Volume c.c.	Per cent. CO_2	Per cent. H	Per cent. CH_4	Per cent. N
1st period	0.84	15.48	40.00	19.05	25.47
2d period	1.15	18.25	52.20	5.48	12.78
3d period	1.18	4.23	73.22	5.93	3.13
Total	3.17				

(To be continued.)

Valuable Clay Deposits in Louisiana. ANON. (*U. S. Geological Survey Press Bulletin*, No. 349, December, 1917.)—The clays of Louisiana have not received a great deal of attention for two reasons. As the principal industry of Louisiana is agriculture, the demand for clay products within the state has not been great; furthermore, most of the local needs for structural material have been supplied by its large and valuable timber resources. Some structural materials have been manufactured from clay in the vicinity of some of the large cities, but Louisiana in 1915 produced a little less than 0.25 per cent. (in value) of the total clay products of the United States.

In a paper entitled "Louisiana Clays," by George C. Matson, just issued as Bulletin 660-E of the United States Geological Survey, Department of the Interior, clays obtained in each of the principal geologic formations of the state are described, and the results of tests made by the Bureau of Standards are given. The paper shows that there are in Louisiana considerable deposits of clay suitable for making common brick, draintile, hollow brick, and the simpler shapes of fireproofing.

A copy of this paper may be obtained by addressing a request for it to the Director, U. S. Geological Survey, Washington, D. C.

OUTLINE OF COLLOID CHEMISTRY.—II.*

BY

WILDER D. BANCROFT,

Professor of Physical Chemistry, Cornell University, Ithaca, N. Y.

ADSORPTION FROM SOLUTION AND COALESCENCE.

ADSORPTION FROM SOLUTION BY SOLID.

SELECTIVE adsorption from a solution by a solid may show itself by relatively more of the dissolved substance being adsorbed than of the solvent, or by relatively less being adsorbed. Both cases are known, but the first one is the more interesting. The decolorizing action of charcoal [1] has been known since 1791. In 1874 Böttger [2] pointed out that infusorial earth will remove all the color from aqueous solutions of some aniline dyes. The adsorption of dyes by hydrous alumina, stannic oxide, and other mordants, as they are called, is of great importance. Here, as in all other cases, the adsorption is selective, some dyes being taken out and others not.[3] Red phosphorus will decolorize a dilute solution of iodine in carbon bisulphide.[4] Hatschek [5] points out that iodides cannot be shown to be present in sea-water by any of the usual tests, and that we owe our supply of iodine to the adsorption of iodides by certain sea-weeds. When making density determinations by weighing a solid in a solution, an error may be introduced because of the solid adsorbing some of the salt.[6] According to Skey,[7] antimony and arsenic can be removed from solutions of their oxides or chlorides in strong hydrochloric acid (with a little tartaric acid in the case of antimony) so that neither of them can be detected by Reinsch's test, though both were easily detected before the adsorption.[8] In 1845

* Based on a paper presented at the meeting of the Section of Physics and Chemistry held Thursday, January 11, 1917.

[1] Cf. Ostwald, "Lehrbuch allgem. Chemie," **1**, 1093 (1891).

[2] *Jour. Chem. Soc.*, **28**, 170 (1875).

[3] Cf. Davison, *Jour. Phys. Chem.*, **17**, 737 (1913).

[4] Sestini, *Gazz. chim. ital.*, **1**, 323 (1871).

[5] "An Introduction to the Physics and Chemistry of Colloids," 6 (1913).

[6] Thoulet, *Comptes rendus*, **99**, 1071 (1884).

[7] *Chem. News*, **17**, 157 (1868); **36**, 6 (1877).

[8] See also Lockemann and Paucke, *Zeit. Kolloidchemie*, **8**, 273 (1911).

Yorke[9] noted the adsorption of lead oxide by filter-paper, while Müller[10] and Weiske[11] have shown that filter-paper takes up such appreciable quantities of barium, strontium, and calcium hydroxides that dilute solutions should not be filtered if they are to be used for quantitative work.

A special phenomenon in connection with adsorption by filter-paper has been studied by Bayley,[12] Lloyd,[13] Gordon,[14] and others. If a drop of salt solution be allowed to fall on a piece of filter-paper the solution will tend to spread. If the salt is adsorbed very strongly it will not spread and we get a relatively wide water-ring. If the salt is not much adsorbed, it will spread out as far as the water. If a strip of filter paper be dipped into a solution we get a similar phenomenon; the water will rise much farther than the salt if the latter is adsorbed strongly. Gordon found that with a M/40 $CuSO_4$ solution the water rose about 9.2 cm. in half an hour and the copper salt only 5.5 cm. With a M/2 solution the copper salt rose 9.2 cm., and so did the water. Ordinary ink shows the phenomenon well with blotting-paper.

Leighton[15] has determined the adsorption of caustic soda, hydrochloric acid, sulphuric acid, and phosphoric acid by purified absorbent cotton. These experiments were interesting in two ways. In the first place, they showed that no compounds were formed. In the second place, data were obtained showing the possible error when determining adsorption. The usual method is to shake a known solution with a weighed amount of the adsorbing solid, pipette off some of the supernatant liquid, and analyze. The amount of adsorption is calculated from the decrease in concentration. This calculation is accurate only in case no liquid is taken up by the solid adsorbing agent. If the cotton adsorbed the alkali and the water in the same ratio in which they occurred in the solution there would be no change in the concentration of the solution and the apparent adsorption would be zero. To avoid this error, Leighton centrifuged the cotton for an hour in a centrifugal rotating about 4000 revolutions per

[9] *Mem. Chem. Soc.*, **2**, 399 (1845).
[10] *Jour. prakt. Chem.*, **83**, 384 (1861).
[11] *Jour. Chem. Soc.*, **30**, 662 (1876).
[12] *Ibid.*, **33**, 304 (1878).
[13] *Chem. News*, **51**, 51 (1885).
[14] *Jour. Phys. Chem.*, **18**, 337 (1914).
[15] *Ibid.*, **20**, 32, 188 (1916).

minute, and then analyzed the cotton This direct or "gravimetric" method will give too high adsorptions unless the centrifuging removes all the unadsorbed solution. On the other hand, the indirect or "titration" method gives too low results unless no water is adsorbed by the cotton at all. Since this last is not true, the results by the titration method are necessarily wrong with cotton, while the results by the gravimetric method may be right. The differences between the two methods may be quite considerable. With a solution of 200 grams NaOH per liter Leighton found an adsorption of 0.27 grams NaOH per gram cotton by the titration method, and of 0.75 gram NaOH by the gravimetric method. The true adsorption lies between these two values. Leighton's data for NaOH are given in Table I.

TABLE I.

Volume of solution = 100 c.c.
Weight of cotton = about 1.0 g.
Time of run = 3 hours.

Solution grams NaOH per liter	Grams NaOH adsorbed per gram cotton		Solution grams NaOH per liter	Grams NaOH adsorbed per gram cotton	
	Gravimetric	Titration		Gravimetric	Titration
474	0.916	....	230	0.664	....
450	.....	0.28	212	0.662	....
427	0.887	....	210	.....	0.19
415	0.875	....	190	0.594	....
400	.....	0.27	189	0.579	....
379	0.846	....	184	0.572	....
350	.....	0.27	175	.....	0.12
323	0.782	....	140	.....	0.08
300	.....	0.27	138	0.461	....
276	0.733	....	125	0.433	....
275	.....	0.25	90	.....	0.01
231	0.665	....	40	.....	0.0

Osaka [16] has made some experiments on the adsorption of potassium and sodium salts by blood charcoal. The charcoal takes up about 85 per cent. of its weight of water when suspended in saturated water vapor at 25°. If no account is taken of this fact a large error may be introduced. When allowance was made for the amount of adsorbed water it was found that the adsorption decreased in the order $I > No_3 > Br > Cl > SO_4$. The potassium salts are adsorbed more strongly than the corresponding

[16] *Mem. Coll. Sci. Kyoto*, 1, 257 (1915).

sodium salts. The numerical values are given in Table II. The percentage adsorptions for normal solutions of KI, KNO_3, KBr, KCl, and K_2SO_4 are approximately 28, 16, 14, 7, and 5 respectively.

An interesting and important case of selective adsorption has been worked out by Lloyd. From fuller's earth he has prepared a hydrous aluminum silicate [17] which adsorbs alkaloids. It has been suggested that the material be called Lloyd's reagent.

TABLE II.

Adsorption of Salts (Milligrams and Milligram Equivalents) per Gram Blood Charcoal.

Concentration of solution in gram equivalent per liter	Salt adsorbed by one gram charcoal		Concentration of solution in gram equivalent per liter	Salt adsorbed by one gram charcoal	
	Milligram	Milligram equivalent		Milligram	Milligram equivalent
	Potassium sulphate			Sodium sulphate	
1.010	51.4	0.59	1.068	40.5	0.57
0.830	45.1	0.52	0.933	37.4	0.53
0.673	37.0	0.42	0.753	31.9	0.45
0.509	29.3	0.34	0.583	25.5	0.36
	Potassium chloride			Sodium chloride	
0.966	68.6	0.92	0.998	47.4	0.81
0.765	50.8	0.68	0.896	44.9	0.77
0.562	41.8	0.56	0.697	35.3	0.60
0.479	33.2	0.45	0.597	29.0	0.49
	Potassium nitrate			Sodium nitrate	
0.977	151.2	1.50	0.978	116.3	1.37
0.817	129.9	1.28	0.816	107.6	1.27
0.654	112.7	1.11	0.647	99.4	1.03
0.491	87.7	0.87	0.484	69.6	0.82
	Potassium iodide			Potassium bromide	
0.967	277.9	1.67	0.970	139.2	1.17
0.833	250.8	1.51	0.717	98.1	0.82
0.622	207.4	1.25	0.526	75.7	0.64
0.464	167.8	1.01	.....	.....	....

Carey Lea [18] has shown that silver idoide adsorbs iodine strongly. It is probably this adsorption which makes silver iodide photographic emulsions apparently less sensitive than the silver bromide emulsions. If so, it should not be hard to overcome that difficulty. Reinders [19] has found that silver chloride crystals contain adsorbed gelatine when crystallizing from an ammoniacal solution to which gelatine has been added. This fact is of great importance

[17] Waldbott, *Jour. Am. Chem. Soc.*, **35**, 837 (1913).

[18] *Am. Jour. Sci.* (3), **33**, 492 (1887).

[19] *Zeit. phys. Chem.*, **77**, 696 (1911).

for the theory of the photographic emulsion.[20] Much other work on adsorption by crystals is to be found in the papers by Marc.[21] The selective nature of the adsorption is shown by the fact that barium sulphate is said to carry down large amounts of barium nitrate and only small quantities of barium chloride.[22] These experiments should be repeated.

On or just back of the beaches at Galveston, Nantucket, and elsewhere there are wells of fresh water, the levels of which correspond approximately with the ocean level. Many people believe that the water in these wells comes from the sea and that the salts have been removed in some mysterious way. Unfortunately this is not true. The water comes from inland, but is backed up by the ocean and does not flow off so rapidly as it otherwise would. If for any reason the outward flow is checked for a sufficient time, the salt from the ocean does work back into the wells. This has been noticed at Galveston when excessive amounts of water have been pumped from the wells.

THE ADSORPTION ISOTHERM.

In all cases which have been studied quantitatively, the form of the adsorption isotherm is similar to that obtained for the adsorption of gases by solids. Consequently an equation of the same type will represent both sets of phenomena. For solutions we write the equation where x is the amount adsorbed by m

$$(x/m)^n = k\,c$$

units of the solid adsorbing agent, c is the concentration of the solution, and n is not necessarily an integer, though experimentally never less than unity. The approximate accuracy of the formula is shown in Freundlich's data,[23] Tables III–V. Other adsorption formulas have been proposed, or discussed by Freundlich,[24] McBain,[25] Schmidt,[26] Georgievics,[27] and others,[28] but no

[20] Bancroft, *Jour. Phys. Chem.*, **17**, 93 (1913).

[21] *Zeit. phys. Chem.*, **61**, 385 (1908); **67**, 470 (1909); **68**, 104 (1909); **73**, 685 (1910); **75**, 710 (1911).

[22] Mitscherlich, *Liebig's Ann.*, **44**, 192 (1842).

[23] "Kapillarchemie," 147 (1909).

[24] *Zeit. phys. Chem.*, **57**, 385 (1907); **59**, 284 (1907).

[25] *Jour. Chem. Soc.*, **91**, 1683 (1910).

[26] *Zeit. phys. Chem.*, **74**, 689 (1910); **77**, 641 (1911); **78**, 667 (1912); **91**, 103 (1916).

[27] *Ibid.*, **83**, 269 (1914).

[28] Marc, *Zeit. phys. Chem.*, **51**, 641 (1913); Dietl, *Monatsheft für Chemie*, **35**, 784 (1914); Trümpler, *Zeit. Kolloidchemie*, **15**, 10 (1914).

formula is strictly accurate, and the simplest one seems the best for the time being. If the curves really bend round parallel to the axis of ordinates, the simple formula is necessarily wrong.

TABLE III.

Distribution of Acetic Acid between Water and Blood Charcoal.

$(x/m)^n = kc$

$n = 2.35$; $\log k = 0.98$

c in mols per liter; x/m in millimols per gram charcoal.

c	x/m found	x/m calc.	$\log k$
0.0181	0.467	0.474	0.966
0.0309	0.624	0.623	1.029
0.0616	0.801	0.798	0.984
0.1259	1.11	1.08	1.006
0.2677	1.55	1.49	1.030
0.4711	2.04	1.90	1.055
0.8817	2.48	2.48	0.981
2.785	3.76	4.04	0.906

TABLE IV.

Distribution of Bromine between Water and Blood Charcoal.

$(x/m)^n = kc$

$n = 2.4$; $\log k = 0.974$

c in millimols per liter; x/m in millimols per gram charcoal.

c	x/m found	x/m calc.	$\log k$
0.92	2.07	2.09	0.965
2.59	3.10	2.96	1.032
6.69	4.27	4.10	1.028
17.08	5.44	5.64	0.930
29.75	6.80	6.80	0.974

TABLE V.

Distribution of Benzoic Acid between Water and Blood Charcoal.

$(x/m)^n = kc$

$n = 2.53$; $\log k = 2.32$

c in millimols per liter; x/m in millimols per gram blood charcoal.

c	x/m found	x/m calc.	$\log k$
6.18	0.437	0.445	2.299
25.00	0.780	0.776	2.329
53.13	1.04	1.04	2.318
117.73	1.44	1.43	2.330

In Table VI are given a list of a few of the systems which have been studied quantitatively. The values for n have undoubtedly been rounded off in most cases. The fact that we get a smooth curve with water, iodine, and starch shows that there is no definite compound, starch iodide.

TABLE VI.

Solvent	Solute	Solid	n	Observer
Alcohol	Iodine	Charcoal	4	Schmidt [1]
Benzene	Iodine	Charcoal	4	Schmidt [1]
Water	Acetic acid	Charcoal	2	Schmidt [1]
Water	Succinic acid	Charcoal	2	Schmidt [1]
Water	Oxalic acid	Charcoal	10	Schmidt [1]
Water	Potassium chloride	Silicic acid	1	
Water	Potassium chloride	Stannic oxide	1	Van Bemmelen [2]
Water	Potassium chloride	Charcoal	1	Lachs and Michaelis [3]
Water	Sulphuric acid	Caseine	1.95	Van Slyke [4]
Water	Indigo carmine	Silk	2	Georgievics [5]
Water	Methylene blue	Cellulose	2	Georgievics [5]
Water	Iodine	Starch	5	Küster [6]
Water	Alizarine	Chromic oxide	3	Biltz [7]
Water	Milk sugar	Charcoal	4.5	Wagner [8]
Water	Cane sugar	Charcoal	8.2	Wagner [8]
Water	Picric acid	Silk	2.7	Walker and Appleyard [9]

[1] *Zeit. phys. Chem.*, **15**, 56 (1894).
[2] *Zeit. anorg. Chem.*, **23**, 113 (1900).
[3] *Zeit. Elektrochemie*, **17**, 2 (1911).
[4] *Am. Chem. Jour.*, **38**, 383 (1897).
[5] *Sitzungsber. Akad. Wiss. Wien.*, **103**, ii b, 589 (1894); **104**, ii, b, 309 (1895); *Zeit. Farbenindustrie*, **2**, 253 (1903).
[6] *Liebig's Ann.*, **283**, 364 (1891).
[7] *Ber. deutsch. chem. Ges.*, **38**, 4143 (1905).
[8] *Zeit. Kolloidchemie*, **8**, 126 (1911).
[9] *Jour. Chem. Soc.*, **69**, 1334 (1896).

ABNORMAL ADSORPTION.

Cameron and Patten [29] find that the distribution of gentian violet between soils and water, or of eosine between quartz and water, can be represented fairly well by exponential formulas; but that flocculation or coarsening of the adsorbing medium is apparently a disturbing factor. That flocculation actually does take place had been shown by Patten [30] in a special set of experiments on quartz flour and dyes. A still more striking case of flocculation and consequent change of adsorption was studied by Lottermoser and Rothe [31] in the adsorption of potassium iodide

[29] *Jour. Phys. Chem.*, **11**, 581 (1907).
[30] *Trans. Am. Electrochem. Soc.*, **10**, 67 (1906).
[31] *Zeit. phys. Chem.*, **62**, 359 (1908).

by silver iodide. For concentrations of potassium iodide up to about N/300 the exponential formula holds fairly well, the exponential factor being a little over 13. Beyond this concentration the amount of adsorption actually decreases with increasing concentration in the water phase. The silver iodide becomes denser and more granular and shows signs of crystallization. On the other hand, silver nitrate is adsorbed by silver iodide without producing this change within the concentrations studied. The exponential factor is 2 for silver nitrate. Freundlich and Schucht [32] found that amorphous mercuric sulphide changes over spontaneously into a crystalline form and then has a decreased power of adsorbing dyes. The adsorption of eosine by hydrous copper oxide varies with changes in the cupric oxide.[33] The cases of abnormal adsorption reported by Evans are apparently due to analytical errors.[34]

In 1899 Lagergren [35] reported the negative adsorption of some chlorides and of ammonium bromide by charcoal, the solution becoming more concentrated after being shaken with the charcoal. Quite recently Osaka [36] found that sodium nitrate, potassium bromide, potassium iodide, and potassium nitrate are adsorbed positively by blood charcoal, while sodium chloride, sodium sulphate, and potassium sulphate are apparently adsorbed negatively. With sodium sulphate the increase in concentration was about one per cent., and was less than that with the other salts. Mathieu [37] observed negative adsorption with a number of dilute solutions when adsorbed by porous plates, membranes, or capillary tubes. With normal solutions the concentrations in the capillary tubes were often only tenth-normal. The difference in concentration increases with decreasing radius of the capillary tubes, and Mathieu considers it quite possible that with very fine tubes water alone would be adsorbed, a conclusion which, as Mathieu himself points out, is of distinct importance for the theory of semipermeable membranes.[38] If this conclusion is true and general,

[32] *Ibid.*, **85**, 660 (1913).
[33] Gilbert, *Jour. Phys. Chem.*, **18**, 592 (1914).
[34] Murray, *Ibid.*, **20**, 621 (1916).
[35] Freundlich, "Kapillarchemie," 165 (1909).
[36] *Mem. Coll. Sci. Kyoto*, **1**, 257 (1915).
[37] *Drude's Ann.*, **9**, 340 (1902).
[38] Cf. Trouton, *Brit. Assn. Reports*, **84**, 288 (1914).

it accounts for the results of Bigelow [39] and of Bartell,[40] who found that osmotic phenomena appeared in porous cups when the pores were sufficiently fine or were clogged sufficiently. It is clear that we can get osmotic phenomena in two distinct ways, depending on whether we have a continuous film or a porous one.[41] In the case of a continuous film it is essential that the solvent shall dissolve in the membrane and that the solute shall not. Since the permeability is not dependent on adsorption, there is no reason why there should be any fundamental difference between the adsorption of a solute which does pass through the membrane and of one which does not pass through. If we have a porous film, we get osmotic phenomena only in case the pore walls adsorb the pure solvent, and the diameter of the pores is so small that the adsorbed film of pure solvent fills the pores full. Under these circumstances the dissolved substance can not pass through the membrane unless adsorbed by the latter. There is therefore an important difference between a solute which does pass through a porous membrane and one that does not, in that the first is adsorbed by the membrane and the second is not.

Kahlenberg [42] has shown that benzene, toluene, and pyridine pass through a rubber membrane very readily, while water does not. This is perfectly natural on the assumption that these liquids dissolve in rubber, but on the basis of pores it is hard to understand why water should not pass through. One might cite the case of the oiled sieve and say that water does not wet rubber, but water does wet rubber. The case of trichloracetic acid is also interesting. When dissolved in benzene it passes readily through a rubber membrane, whereas it passes very slowly when dissolved in water. This is as it should be if we are dealing with solution, but it is hard to explain if we are dealing with adsorption. While nothing is proved, I am inclined to think that a rubber membrane is not a porous one in the sense that Bartell's clogged plate is, and I believe, therefore, that, when a rubber film acts as a semipermeable membrane, the solvent dissolves in the rubber and passes through it essentially in that way. There are no satis-

[39] *Jour. Am. Chem. Soc.*, **29**, 1576, 1675 (1907); **31**, 1194 (1909).

[40] *Jour. Phys. Chem.*, **15**, 659 (1911); **16**, 318 (1912); *Jour. Am. Chem. Soc.*, **36**, 646 (1914); **38**, 1029, 1036 (1916).

[41] Bancroft, *Jour. Phys. Chem.*, **21**, 441 (1917).

[42] *Jour. Phys. Chem.*, **10**, 141 (1906).

factory data in regard to the copper ferrocyanide membrane, but it seems better for the present to consider it as like the rubber membrane.

REVERSIBILITY OF EQUILIBRIUM.

To be certain that the equilibrium represented by the adsorption isotherm is a reversible one, it should be reached from both sides. As a rule, that is not done, but Freundlich [43] has made a couple of experiments to show that the same end-point is actually reached. For the distribution of acetic acid between charcoal and water, he obtained a concentration in the water of N/16.47 when he shook one gram of charcoal with 100 c.c. of N/14.53 solution, and a concentration of N/16.49 when he shook one gram of charcoal with 50 c.c. of a N/7.27 solution and then added 50 c.c. water. For the distribution of benzoic acid between charcoal and benzene, a similar proceeding with other concentrations gave him the two final values of N/8.5 and N/8.48. In some cases equilibrium is reached very rapidly from both sides, and in others not.[44] While the adsorption equilibrium is theoretically a reversible one, there are conditions under which there may be apparent or actual irreversibility. If charcoal takes a dye out of solution to such an extent as to decolorize the water practically, no amount of washing with water will give a colored solution, even though dye is being taken out all the time.[45] In this case the adsorption is strictly reversible, and the difficulty was in the interpretation of the results.

There is one experiment which I always like to try, because it proves something whichever way it goes. A solution of iodine in water is shaken with bone-black, filtered, and tested with starch paste. If the colorless solution does not turn the starch blue, the experiment shows how completely charcoal extracts iodine from aqueous solution. If the starch turns blue, the experiment shows that the solution, though apparently colorless, still contains iodine, which can be detected by means of the sensitive starch test.

If the adsorbing substance changes through agglomeration, crystallization, or in any other way, its specific adsorbing power

[43] "Kapillarchemie," 148 (1909).

[44] Freundlich, *Zeit. phys. Chem.*, **57**, 388 (1906); Ostwald, *Lehrbuch allgem. Chemie*, 1, 1096 (1891); Schmidt, *Zeit. phys. Chem.*, **74**, 708 (1910).

[45] Freundlich and Neumann, *Ibid.*, **67**, 538 (1900).

will change, and the adsorbed substance will be held either more or less firmly, as the case may be. Some instances of this have already been cited under abnormal adsorption. The adsorbed substance may also change on standing or on heating, in which case we shall have an apparent irreversibility, though we are really dealing, as before, with a new reversible equilibrium. This case occurs very frequently in dyeing.[46]

SPECIFICITY OF ADSORPTION.

Since adsorption is essentially specific, the amount of adsorption will necessarily vary with the nature of the adsorbing agent, the liquid, and the substance to be adsorbed. In illustration of this, Freundlich [47] cites the experiments of Wöhler, Pluddeman and Wöhler [48] to the effect that charcoal and ferric oxide adsorb benzoic acid about ten times as strongly as acetic acid, while chromium oxide adsorbs the two acids about equally, and platinum black adsorbs acetic acid a little, but benzoic acid practically not at all. All salts seem to show distinct adsorption for their own ions. Thus silver bromide adsorbs silver nitrate or potassium bromide, but not potassium nitrate. Charcoal adsorbs both acid and basic dyes. Alumina takes up many acid dyes readily and not the basic dyes; silica and tannin adsorb the basic dyes more readily than acid dyes. Wool adsorbs many dyes strongly without a mordant, and cotton relatively few. What is known as Schulze's law [49] is that the power of active ions to precipitate colloidal solutions is a function of its valence, or of the number of electrical charges which it carries. Since the precipitating power, in the cases studied by Schulze, depends on the degree of adsorption, it follows that, in so far as Schulze's law holds, a trivalent ion will be adsorbed more strongly than a bivalent ion, and the latter more strongly than a univalent one. Schulze's law is merely a first approximation.[50] Everybody recognizes that hydrogen and hydroxyl ions are not to be classed with the other univalent ions, because they are usually adsorbed much more strongly,[51] and everybody recognizes that there are other excep-

[46] Lake, *Jour. Phys. Chem.*, **20**, 761 (1916).
[47] "Kapillarchemie," 155 (1909).
[48] *Zeit. phys. Chem.*, **62**, 664 1908).
[49] Schulze, *Jour. prakt. Chem.* (2), **25**, 43 (1882); **27**, 320 (1884).
[50] Bancroft, *Jour. Phys. Chem.*, **19**, 363 (1915).
[51] Freundlich, "Kapillarchemie," 354 (1909).

tions. In case of doubt, it is generally safe to assume that an ion of higher valence will be adsorbed more strongly than one of lower valence, but it is a mistake to consider this so-called law as anything more than a guide. For instance, Osaka [52] found that charcoal adsorbed potassium salts in the following order when the salts were present in equivalent concentrations: $KI > KNO_3 > KBr > KCl > K_2SO_4$, from which it follows that, for equivalent concentration, the sulphate ion is adsorbed the least of all. If we were to compare molecular concentrations the sulphate ion would be adsorbed as strongly as the bromide ion, but less than the nitrate or the iodide ion. Davis [53] found that the order of adsorption of iodine from different liquids was not the same with different kinds of charcoal. With animal charcoal there was decreasing adsorption in the order: chloroform, alcohol, ethyl acetate, benzene, and toluene; with sugar charcoal the adsorption decreased in the order: chloroform, toluene, ethyl acetate, benzene, and alcohol; whereas for cocoanut charcoal the order was toluene, chloroform, benzene, alcohol, and ethyl acetate. There are at least two factors governing the effect of the solvent. The more soluble the dissolved substance is in a given solvent, the less readily will it be adsorbed, provided we can neglect the adsorption of the solvent itself by the solid. There are many illustrations of this, but one will suffice. Charcoal will decolorize aqueous solutions of iodine or of methyl violet, but alcohol will extract the color from the charcoal. The solubility cannot be the sole factor, however, because then the solvents could always be arranged in the same order for the same solute, regardless of the nature of the adsorbing agent. This is disproved absolutely by the experiments of Davis. One other factor is the adsorption of the solvent by the adsorbing agent. This factor was not taken into account at all by Davis, whose data are therefore not sufficient to enable us to tell whether there are other factors to be considered.

In so far as adsorption is accompanied by an evolution of heat, the amount of adsorption must decrease with rising temperature. This is found to be the case experimentally, but the change is often a very small one. In some cases there is an apparently

[52] Osaka, *Mem. Coll. Sci. Kyoto*, **1**, 267 (1915).
[53] *Jour. Chem. Soc.*, **91**, 1682 (1907).

large increase in adsorption with rising temperature. Thus wool takes up very little acid violet at 20° and a great deal at about 95°. Experiments showed [54] that this adsorption is not reversible, for the acid violet adsorbed at the higher temperature cannot be washed out to any extent at 20°. After adsorption the dye agglomerates or changes so that it becomes practically insoluble, and consequently the wool takes up more dye.

ADSORPTION OF SEVERAL SOLUTES.

Some years ago there was a widespread rumor that strychnine had been added to a certain breakfast cereal to make it more appetizing. The report was false and not even new, for in 1852 it was alleged that strychnine was being added to certain English pale ales. In order to show that strychnine could be detected in beer if present, Graham and Hofmann [55] shook two ounces of animal charcoal with half a gallon of beer to which ½ grain of strychnine had been added. The strychnine was removed practically completely by the charcoal, and was extracted from that with alcohol and identified.

Skey [56] reports that dilute sulphuric acid can be freed from traces of nitric acid by shaking with charcoal, while concentrated sulphuric acid cannot be. Dudley [57] showed that the rank and disagreeable odor of raw whiskey can be removed by leaching through charcoal. Schmidt [58] has studied the simultaneous adsorption of iodine and acetic acid by charcoal from solutions in water and in ethyl acetate. With both solvents less of each substance was adsorbed than if the other had not been present. Schmidt believes that this is general, but this statement is undoubtedly too broad, though it holds in many cases. Freundlich and Masius [59] studied the adsorption of pairs of organic acids and obtained results similar to those of Schmidt. They also found that the acid, which is adsorbed more, is displaced the less when the two acids are present in the solution. These experiments throw light on Skey's experiments. With increasing relative concentration of sulphuric acid, we should expect an increasing

[54] Lake, *Jour. Phys. Chem.*, **20**, 761 (1916).
[55] *Jour. Chem. Soc.*, **5**, 173 (1853).
[56] *Chem. News*, **17**, 217 (1886).
[57] *Jour. Am. Chem. Soc.*, **30**, 1784 (1908).
[58] *Zeit. phys. Chem.*, **74**, 730 (1910).
[59] "Van Bemmelen Gedenkboek," 88 (1910).

displacement of nitric acid from the charcoal, which is what actually occurred. Lachs and Michaelis[60] found that caustic potash cut down very much the adsorption of potassium chloride by charcoal from water. In other words, the presence of the strongly adsorbed hydroxyl ion decreased the adsorption of the chloride very much. They also found that if sulphuric acid is added in small amounts to the chloride solution the adsorption of chloride ion is increased markedly. This is in accord with the results of Osaka,[61] that potassium chloride is adsorbed more than potassium sulphate, sodium chloride than sodium sulphate, and, presumably, hydrochloric acid than sulphuric acid.

Thorium salts cut down the adsorption of uranium X by charcoal,[62] and acetone and acetic acid decrease the adsorption of grape-sugar by charcoal,[63] but albumin and acetone have no effect each on the other, nor does one acid dye apparently displace another on wool or silk.[64]

CHEMICAL ACTION.

Selective adsorption connotes the possibility of chemical decomposition as a result of adsorption.[65] If a given solid adsorbs a base more strongly than an acid, for instance, there will be a tendency for the salt to hydrolyze, the base being then adsorbed to a greater extent than the acid. Theoretically there is always some hydrolysis even with sodium chloride and water, according to the equation,

$$Na^{\cdot} + Cl' + H_2O \rightleftharpoons Na^{\cdot} + OH' + H^{\cdot} + Cl'$$

but this reaction does not run far, because caustic soda and hydrochloric acid are strong electrolytes, and we cannot have a high simultaneous concentration of hydrogen and hydroxyl ions. If the caustic soda is removed by adsorption, either of hydroxyl ion or of undissociated sodium hydroxide, the hydrolysis will go farther. How complete the hydrolysis will be depends on the degree to which the base is adsorbed and on the strength of the unadsorbed acid. Any acid will tend to react with adsorbed caustic soda, but the tendency will be greater the stronger the

[60] *Zeit. Elektrochemie*, **17**, 1 (1911).
[61] *Mem. Coll. Sci. Kyoto*, **1**, 267 (1915).
[62] Freundlich and Kaempfer, *Zeit. phys. Chem.*, **90**, 681 (1915).
[63] Rona and Michaelis, *Biochem. Zeit.*, **16**, 499 (1909).
[64] Lake, *Jour. Phys. Chem.*, **20**, 761 (1916).
[65] Bancroft, *Ibid.*, **18**, 5 (1914).

acid. We thus see that a neutral solution will become acid if shaken with a solid which adsorbs the base more strongly than the acid, that it will become alkaline if the solid adsorbs the acid much more strongly than the base, and that it will remain neutral in case the solid does not adsorb either base or acid at all, or in case it adsorbs the two in practically equivalent quantities. The amount of base or acid taken up from a salt solution will be greater the weaker the unadsorbed acid or base. The experiments of Liebermann [66] show clearly that the decomposition by charcoal is greater with salts of weak acids. Freundlich and Masius [67] have studied the adsorption of aniline benzoate and aniline acetate by charcoal. It so happens that aniline is adsorbed less strongly than benzoic acid by charcoal and more strongly than acetic acid. From a solution of aniline benzoate, therefore, charcoal adsorbs relatively more benzoic acid than aniline, while more aniline than acetic acid is adsorbed from an aniline acetate solution. Skraup [68] dipped filter-paper into a lead acetate solution and found that the acetic acid rose much higher than did the lead, which we know to be adsorbed strongly.[69]

The becoming acid or alkaline of a solution is not necessarily connected with any hypothetical acidity or alkalinity of the adsorbing substance. If fuller's earth be shaken with water and then filtered, the filtrate is neutral to litmus paper [70] or phenolphthalein, showing that no soluble base or acid is present. If fuller's earth be shaken with a sodium chloride solution and filtered, the filtrate is acid to litmus or to phenolphthalein. This is because fuller's earth has adsorbed the base. If one presses litmus paper against moistened fuller's earth, the litmus paper turns red, and if one adds fuller's earth to a fairly alkaline solution of phenolphthalein, the red color disappears. This is not because fuller's earth is acid, but because it takes the base from the sodium chloride, the litmus, or the phenolphthalein. Caseine is practically insoluble in pure water, and the filtrate is neutral to litmus paper. If moistened litmus paper be pressed against caseine, the latter adsorbs alkali from the paper, which, of course, turns red. The adsorption

[66] *Sitzungsber. Akad. Wiss. Wien*, **74**, 331 (1876).
[67] "Van Bemmelen Gedenkboek," 100 (1910).
[68] *Zeit. Kolloidchemie*, **6**, 253 (1910).
[69] Yorke, *Mem. Chem. Soc.*, **2**, 399 (1845).
[70] Cf. Cameron, *Jour. Phys. Chem.*, **14**, 400 (1910).

of alkali is so marked that caseine will set free carbon dioxide from carbonates and bicarbonates. It is not surprising, therefore, that people have considered caseine as an acid and have not perceived that the setting free of carbon dioxide is the result of selective adsorption. The bearing of this on the question of soil acidity has been discussed by Cameron.[71] A statement of the other side of the question has been given by Truog.[72]

Silk has such a marked selective adsorption for rosaniline (magenta) that it will not only decompose the hydrochloride, leaving the acid behind, but will also convert the carbinol base back into the color base in presence of an excess of ammonia,[73] the silk being dyed red from a colorless ammoniacal solution. This is the more remarkable because the free color base is instable and cannot be isolated in a pure state. This makes it seem certain that silk stabilizes the free color base. Another similar instance is the mordanting of wool with copper salts, coloring it green. This green does not change to black when the wool is heated to boiling, though hydrous copper oxide by itself changes very readily. Blucher and Farnau[74] have extended Tommasi's[75] experiments on the stabilization of hydrous copper oxide by manganese salts and find that a number of other metallic hydroxides are also effective. Bayliss[76] has obtained results, which indicate that alumina stabilizes the free acid of Congo red, and Schaposchnikoff and Bogojawlevski[77] have isolated this metastable form by allowing the pyridine salt to effloresce. Reference has already been made to the stabilization of a higher iron oxide by iron in the case of passive iron.

In the case of dyeing with acid or basic dyes we have an admirable illustration of the fact, first recognized by Lachs and Michaelis[78] and by Estrup,[79] that an anion is more readily

[71] *Jour. Phys. Chem.*, **14**, 399 (1910).

[72] *Ibid.*, **20**, 457 (1916).

[73] Jacquemin, *Comptes rendus*, **82**, 261 (1876); see also Mills, *Jour. Chem. Soc.*, **35**, 27 (1879); Fortuyn, *Zeit. phys. Chem.*, **90**, 236 (1915).

[74] *Jour. Phys. Chem.*, **18**, 629 (1914).

[75] Tommasi, *Bull. Soc. chim. Paris* (2), **37**, 197 (1882); *Comptes rendus*, **99**, 37 (1884).

[76] *Proc. Roy. Soc.*, **84B**, 881 (1911).

[77] *Zeit. Farbenindustrie* (1913).

[78] *Zeit. Elektrochemie*, **17**, 1, 917 (1911).

[79] *Ibid.*, **11**, 8 (1912), **14**, 8 (1914).

adsorbed in presence of a readily adsorbed cation, and a cation in presence of a readily adsorbed anion. In an acid dye the color group is in the acid radical, and in a basic dye it is in the basic radical. An acid dye will therefore be taken up more readily in an acid solution than in a neutral solution, and will be taken up least in an alkaline solution. A readily adsorbed anion will decrease the amount of dye taken up, and a readily adsorbed cation will increase the amount of dye taken up. With a basic dye the reverse will be true. The dye will be taken up most readily in an alkaline solution, but may be taken up in a neutral or acid solution. A readily adsorbed cation will cut down the adsorption of the dye, and a readily adsorbed anion will increase it.[80] These generalizations appear to hold in all the cases studied so far.[81] Substantive dyes form colloidal solutions, and the question of stability is an important one.

When discussing the adsorption of gases by solids reference was made to cases of so-called contact catalysis. With solutions the effect of contact materials is as yet relatively unimportant. Lassar-Cohn[82] gives a few instances where yields have been increased by the use of porous masses. Gurwitsch[83] reports that amylene polymerizes readily on standing in contact with "floridin," which is a hydrous silicate of some sort. Richardson[84] believes that petroleum and bitumens are formed by the polymerizing or condensing action of clays or sands.

A case which has been studied a great deal quantitatively is the decomposition of hydrogen peroxide solutions by platinum. One of the most interesting things about this reaction is its sensitiveness to so-called poisons.[85] The rate of decomposition of hydrogen peroxide by a given solution of colloidal platinum is reduced approximately to one-half by M/20 000 000 HCN, M/2 000 000 $HgCl_2$, and M/300 000 H_2S. It has also been

[80] Bancroft, *Jour. Phys. Chem.*, **18**, 1, 118 (1914).

[81] Pelet-Jolivet, "Die Theorie des "Färbeprozesses," 95, 118, 149 (1910); Davison, *Jour. Phys. Chem.*, **17**, 737 (1913); Lake, *Ibid.*, **20**, 785 (1916).

[82] "Arbeitsmethoden für organisch-chemische Laboratorien," 584, 923, 1079 (1903).

[83] *Zeit. Kolloidchemie*, **11**, 18 (1912).

[84] *Jour. Ind. Eng. Chem.*, **8**, 4 (1916); *Met. Chem. Eng.*, **16**, 25 (1917).

[85] Bredig and von Berneck, *Zeit. phys. Chem.*, **31**, 258 (1899); Bredig and Ikeda, *Ibid.*, **37**, 1 (1901).

shown by Schönbein[86] that these same substances cut down the catalytic action of red blood-corpuscles on hydrogen peroxide. In Table VII are given data[87] for the concentrations necessary to cut down the rate of decomposition of hydrogen peroxide to one-half in the case of colloidal platinum and of hæmase, the active enzyme in the red blood-corpuscles. While many of the substances that cut down the platinum catalysis also decrease the catalytic action of hæmase, there are many cases where no paral-

TABLE VII.

Concentrations at which Poisons reduce the Rate of the Catalytic Decomposition of Hydrogen Peroxide approximately to one-half.

Poison	Colloidal platinum	Hæmase
H_2S	M/300 000	M/1 000 000
HCN	M/20 000 000	M/1 000 000
$HgCl_2$	M/2 000 000	M/2 000 000
$HgBr_2$	.....	M/300 000
$Hg(CN)_2$	M/200 000	M/300 000
I_2 in KI	M/5 000 000	M/50 000
$NH_2OH \cdot HCl$	M/25 000	M/80 000
Phenyl hydrazine	.....	M/20 000
Aniline	M/5000	M/400
Arsenious acid	M/50	No poisoning at M/2000
CO	Very poisonous	No poisoning
HCl	M/3000	M/100 000
NH_4Cl	M/200	M/1000
HNO_3	No poisoning	M/250 000
H_2SO_4	No poisoning	M/50 000
KNO_3	No poisoning	M/40 000 at 0°
$KClO_3$	Slight poisoning?	M/40 000 at 0°

lelism occurs. Thus carbon monoxide is very toxic to platinum and has no effect on hæmase. On the other hand, nitric acid, sulphuric acid, potassium nitrate, and potassium chlorate have practically no effect on platinum and are quite toxic to hæmase. Even when there is a general parallelism, one must not follow it too closely. With platinum the prussic acid solution has one-tenth the concentration of the mercuric chloride solution, while with hæmase it has double the concentration. The tabulated

[86] *Jour. prakt. Chem.*, **105**, 202 (1868).

[87] Senter, *Zeit. phys. Chem.*, **51**, 701 (1905).

concentration for mercuric chloride is the same as for hæmase, while that for iodine dissolved in KI is one hundred times as great for hæmase as for platinum. Kastle and Loevenhart [88] point out that prussic acid is a strong poison for colloidal platinum and silver, but accelerates the catalysis of hydrogen peroxide by iron and copper.

It is probable that the poisons are adsorbed strongly by the catalytic agent [89] and therefore prevent the adsorption of hydrogen peroxide. This adsorption will be specific and will therefore not be the same quantitatively for different catalytic agents. On the other hand, there may well be a qualitative agreement in some or even in many cases.

It would seem natural that a colloidal metal, with its enormous surface, would have a greater catalytic action than an equal weight of smooth foil, and this is usually true. Thus Jablczynski[90] found that platinized platinum decomposes chromous chloride three times as fast and hydrogen peroxide one hundred times as fast as does smooth platinum foil. On the other hand, Rosnyak [91] claims that the catalytic action of platinum on hydrogen peroxide decreases with increasing dispersity (fineness) of the platinum, and Felgate [92] states that pulverulent nickel reduces nitric oxide, while colloidal nickel does not. In both these cases it is probable that some factor has been overlooked or not stated. The more finely divided the platinum the more likely the surface is to be coated with oxide, and it does not follow at all that the catalytic action of metallic platinum is the same as that of an oxide of platinum. If the platinum is kept in suspension by means of gelatine or some similar substance, the adsorbed gelatine will probably decrease the adsorption of the reacting substances, and this may more than counterbalance the increased effectiveness due to increased surface. In the hydrogenation of oils, nickel in some form is apparently the catalytic agent most commonly used.

[88] *Am. Chem. Jour.*, **29**, 397 (1903).
[89] Bancroft, *Jour. Phys. Chem.*, **21**, 734 (1917).
[90] *Zeit. phys. Chem.*, **64**, 751 (1908).
[91] *Ibid.*, **85**, 68 (1913).
[92] *Chem News*, **108**, 178 (1913).

ADSORPTION FROM SOLUTION BY LIQUID.

There is no reason why there should not be adsorption from a solution by a liquid just as well as by a solid, except that the matter is complicated by the possibility of the solute dissolving in the second liquid. An interesting case of such adsorption was studied by Wilson and others.[93] If a drop of chloroform or other organic liquid be placed under water in a dish and alkali be added, the drop flattens out, becoming rounder again when the solution is acidified. This change can be repeated apparently indefinitely. While the flattening of the organic liquid is clearly due to a change in surface tension, it cannot depend on the absolute surface tension of the water phase, because Wilson found the effect of alkali to be the same qualitatively whether sodium chloride was present or not, whereas the addition of salt increases the surface tension of the water phase. What happens is that hydroxyl is adsorbed at the dineric interface, lowering the surface tension and causing the organic liquid to flatten. This is confirmed by the experiments of von Lerch,[94] who determined the surface tension between benzene and aqueous solutions by means of the rise in capillary tubes. The adsorption of hydroxyl means practically a concentrating of alkali at the surface of the organic liquid, and consequently a closely adhering film of water. This accounts for Wilson's observation that the drops of chloroform are wetted readily by an alkaline solution. The presence of a surface film of caustic soda solution also accounts for the decreased mobility observed by Wilson.

Patrick[95] has studied the adsorption of new fuchsine, picric acid, salicylic acid, and mercurous sulphate from aqueous solutions by mercury. In all four cases the amounts adsorbed varied with the concentration, approximately, according to an exponential formula, and in all four cases the surface tension of the mercury was lowered by the adsorption.

ADSORPTION AND SURFACE TENSION.

When a substance dissolves in a liquid, the surface tension at the liquid-vapor surface changes, increasing in some cases and

[93] *Jour. Chem. Soc.*, **1**, 174 (1849); Swan, *Phil. Mag.* (3), **33**, 36 (1848); Twomey, *Jour. Phys. Chem.*, **19**, 360 (1915).

[94] *Drude's Ann.*, **9**, 434 (1902).

[95] *Zeit. phys. Chem.*, **8**, 545 (1914).

decreasing in others. Two solutions of the same density will not have the same surface tension. For this reason a hydrometer graduated for sulphuric acid solutions will not be accurate for hydrochloric acid solutions, because the amounts of solution which will rise up the stem will depend on the surface tensions and will therefore not be the same in the two cases. The surface tensions of solutions usually lie between the surface tensions of the constituents; but this is not necessarily true.[96] Röntgen and Schneider[97] found a maximum surface tension for sulphuric acid and water at about 48 per cent. H_2SO_4. Whatmough[98] obtained minima for a number of pairs of liquids. The change in surface tension with a solution is also accompanied by a change in concentration, the surface film of the solution having a different concentration from the mass of the liquid. The simple rule in regard to this is that the concentration in the film tends to change so as to decrease the surface tension.[99] Consequently the surface film will be more dilute than the mass of the solution if the dissolved substance increases the surface tension, and will be more concentrated than it if the solute lowers the surface tension of the solution. An equilibrium will be reached when the change in the surface tension is balanced by the difference of osmotic pressure between the surface film and the mass of the solution, always provided that we are dealing with a true solution. This can be expressed mathematically by the equation[100]

$$\Gamma = -\frac{d\alpha}{d\mu}$$

where α is the interfacial tension, μ is the chemical potential of the dissolved substance in the aqueous phrase, Γ is the mass of solute per unit area of interface (unspecified thickness) in excess of that corresponding to the concentration in the mass of the solution. In other words, Γ is the amount of solute adsorbed per unit area of interface in the interfacial transition layer of unspecified thickness. If the laws of dilute solutions apply, the preceding equations may be written

$$\Gamma = -\frac{C}{RT}\cdot\frac{d\alpha}{dc}.$$

[96] See Freundlich, "Kapillarchemie," 58 (1909).
[97] *Wied. Ann.*, **29**, 165 (1886).
[98] *Zeit. phys. Chem.*, **39**, 129 (1902).
[99] J. Willard Gibbs, *Scientific Papers*, **1**, 219.
[100] Cf. Donnan and Barker, *Proc. Roy. Soc.*, **85A**, 557 (1911).

It is to be noted that these two equations apply only to a substance which is really in solution, a point which is apt to be overlooked in papers on colloids. On the other hand, there are many substances, such as soap, saponine, and gelatine, which are probably not soluble in water to any appreciable extent, but which form apparent or colloidal solutions with surface tensions lower than those of pure water. In these cases the concentration of the added substance will be higher in the surface film than in the mass of the liquid, but the Gibbs formula will not apply. As a matter of fact, the adsorptions, in the surface are 20 to 100 times those calculated from the formula with sodium glychocholate, Congo red, methyl orange, and sodium oleate.[101] Owing to the extreme and unknown thinness of the surface film, it has proved impossible so far to show the change of concentration with any true solution by means of direct analysis. An approximation has been obtained by measuring the surface tension through the drop number. The thickness of the transition layer probably varies in extreme cases from about 1 to 200 $\mu\mu$, being usually fairly near the smaller number.

If the difference in concentration between the mass of the solution and the surface layer is set up slowly, one ought to get one value for the surface tension when equilibrium is reached and another one if measurements are made rapidly on a fresh surface. This has been done experimentally by Lord Rayleigh,[102] though not for a true solution. His data have been recalculated by Freundlich,[103] who added some of his own. They are given in Table VIII. Except in the case of pure water, the surface tensions by the static method are higher than that of pure water in the case of the two very dilute sodium oleate solutions. Lord Rayleigh did not discuss this point, and Freundlich leaves it untouched. In the actual measurements an error of about 2 per cent. would account for the difference, which may be due to experimental error. There is another possibility: that the sodium oleate is completely hydrolyzed in the dilute solutions, and that what is measured by the dynamic method is really the surface tension of a caustic soda solution.

[101] Willows and Hatschek, "Surface Tension and Surface Energy," 46 (1915).

[102] *Proc. Roy. Soc.*, **47**, 281 (1890).

[103] "Kapillarchemie," 56 (1909).

From the fact that the lowering of the surface tension is accompanied by an increase in the concentration of the surface film of a true solution, Freundlich [104] draws the conclusion that this is true in all cases, and that if a dissolved substance lowers the surface between the solid and the solution—whatever one may mean by that—the dissolved substance is adsorbed; conversely, that the dissolved substance is adsorbed only in case it lowers the surface tension at the interface. The conclusion may or may not be right, but the logic is faulty, because the two cases are

TABLE VIII.

Static and Dynamic Surface Tensions of Solutions at Room Temperature.

Solution	Concentration, Per cent.	Surface tension in dynes/cm.	
		Static	Dynamic
Water.....	.....	75	75
Sodium oleate.....	0.025	55	79
Sodium oleate.....	0.25	26	79
Sodium oleate.....	1.25	26	62
Sodium oleate.....	2.5	26	58
Saponin.....	.....	52	73
Heptylic acid.....	0.005N	54	68

not parallel. The Gibbs relation holds for a true solution, where the difference of concentration is entirely inside the solution phase. Freundlich is extending the relation to a heterogeneous system in which the adsorbed substance is presumably on the outer surface of the solid and by definition cannot diffuse into it, because we should then have a solid solution. It is very difficult to prove or disprove Freundlich's conclusion experimentally, but it is a great pity to have people believe, as many now do, that the generalization is based on sound thermodynamics.

BROWNIAN MOVEMENTS.

If a stone be dropped into water, it sinks rapidly; but if it be broken into small pieces, the surface is much greater and consequently the pieces sink more slowly. If the stone were ground into very fine particles, we should expect them to sink very slowly, the rate being a function of the diameter and the density of the particles. A formula has been deduced by

[104] *Zeit. phys. Chem.*, **57**, 424 (1907).

Stokes,[105] which should hold after a constant rate of fall is reached. V is the constant rate of fall, r the radius of the

$$V = \frac{2.2^2(S-S')g}{9\eta}$$

particles, S their specific gravity, S' the specific gravity of the liquid, η its viscosity coefficient, and g the gravitational constant. Hatschek [106] has calculated the results for several special cases.[107] For particles of 1μ radius the rate of fall in water is calculated to be 2.4 mm. per minute. With gold particles of $10\mu\mu$ radius the calculated rate of settling in water is about 10 mm. per month. For a particle of $10\ \mu\mu$ radius and a specific gravity of only 3 the calculated rate is about 1 mm. per month. The formula does not hold experimentally when the particles are very fine. Eboll [108] states that ultramarine will stay suspended for months when obtained in a very finely divided state by grinding and elutriation. Mülhäuser [109] found that when very finely ground carborundum powder is treated with water a portion does not settle in months, and behaves in that respect like colloidal silver. Brewer [110] pointed out the slow rate at which clays settle, and raised the question whether extremely finely divided particles settle at all. If they do not, there must be some factor which neutralizes the action of gravity more or less completely. The experiments of an English botanist named Brown [111] furnish the clue to the difficulty, though the importance of these experiments was not appreciated until very much later. A microscopic study showed that extremely minute particles of any solid substance suspended in water exhibit irregular motions remarkably like those of bacteria. These movements of suspended particles are known as Brownian movements and are apparently due to the bombardment of the suspended particles by the molecules of the liquid.[112] From Exner's experiments [113] it appears that par-

[105] "Mathematical and Physical Papers," **3**, 1 (1901).

[106] "An Introduction to the Physics and Chemistry of Colloids," 24 (1913).

[107] Elutriation, or the difference in the rate of settling, is much used in grading such powders as emery, carborundum, ultramarine, kaolin, etc.

[108] *Ber. deutsch. chem. Ges.*, **16**, 2429 (1883).

[109] *Zeit. anorg. Chem.*, **5**, 117 (1894).

[110] *Mem. Nat. Acad. Sci.*, **2**, 165 (1884); *Am. Jour. Sci.* (3), **29**, 1 (1885).

[111] *Phil. Mag.*, **4**, 161 (1828); **6**, 161 (1829).

[112] *Jour. de Phys.* (2), **7**, 561 (1888); *Comptes rendus*, **109**, 102 (1889).

[113] *Sitzungsber. Akad. Wiss. Wien.*, **56**, ii, 116 (1867).

ticles with a diameter larger than 4 μ show no perceptible Brownian movement in water. Particles smaller than 0.1 μ begin to show lively movements,[114] while particles with diameters of about 10 $\mu\mu$ give apparent trajectories up to 20 $\mu\mu$. In more viscous liquids the motion is, of course, less. The bombardment of the suspended particles will tend to give a uniform distribution. Under the influence of gravity we should get an increased concentration in the lower part of the vessel.[115]

" Let us suppose that it is possible to obtain an emulsion with the granules all identical, an emulsion which I will call, for shortness, *uniform*. It appeared to me at first intuitively that the granules of such an emulsion should distribute themselves as a function of the height in the same manner as the molecules of a gas under the influence of gravity. Just as the air is more dense at sea-level than on a mountain-top, so the granules of an emulsion, whatever may be their initial distribution, will attain a permanent state when the concentration will go on diminishing as a function of the height from the lower layers, and the law of rarefaction will be the same as for air.[116] " To test this hypothesis, Perrin prepared a uniform suspension of purified gamboge in water by means of fractional centrifuging. The results confirmed the hypothesis. With gamboge particles 0.3 μ in diameter a rise of 30 μ was sufficient to lower the concentration to a tenth of its value, 10 μ in the gamboge suspension being equivalent to six kilometers in the air. Similar results were obtained with mastic in water. Satisfactory results have also been obtained by Zangger [117] for drops of mercury, by Brillouin [118] for gamboge in glycerol solutions having a viscosity 160 times that of water, and by Iljin.[119] The mathematical theory has been developed by Einstein,[120] Smoluchowski,[121] and others. Perrin [122] considers that " the Brownian movement offers us, on a different scale, the faithful picture of the movements possessed, for example, by the

[114] Zsigmondy, " Kolloidchemie," **18** (1912).
[115] Perrin, " Brownian Movement and Molecular Reality," 22 (1910).
[116] Perrin, " Brownian Movement and Molecular Reality," 43 (1910).
[117] *Zeit. Kolloidchemie*, **7**, 216 (1911).
[118] *Ann. Chim. Phys.* (8), **27**, 412 (1912).
[119] *Zeit. phys. Chem.*, **83**, 592 (1913).
[120] *Drude's Ann.*, **17**, 549 (1905), **19**, 289, 371 (1906).
[121] *Ibid.*, **21**, 756 (1906).
[122] Perrin, " Brownian Movement and Molecular Reality," 46 (1910).

molecules of oxygen dissolved in the water of a lake, which, encountering one another only rarely, change their direction and speed by virtue of their impacts with the molecules of the solvent. It may be interesting to observe that the largest of the granules, for which I have found the laws of perfect gases followed, are already visible in sunlight under a strong lens. They behave as the molecules of a perfect gas, of which the gram molecule would weigh 200,000 tons."

It seems to be accepted pretty generally that the work of Perrin, Svedberg, and others has established the practical continuity between suspended particles and dissolved substances, but this seems to be an over-hasty conclusion. The molecular weight of a dissolved substance, as calculated from the osmotic pressure, means something quite definite. The molecular weight of a suspended particle, as calculated from any of Einstein's formulas, means something entirely different, if it means anything at all. We can determine the molecular weight of benzene approximately from the measurement of the surface tension, but it is absurd to say that suspending fine drops of benzene in water causes the molecular weight of benzene to become equal to 200,000 tons. We are talking about entirely different things in the two cases. What we mean is that liquid benzene has a molecular weight of 78, and that liquid benzene suspended in water behaves, or may behave, as if it were a dissolved substance having a molecular weight of 200,000 tons, more or less. As a matter of fact, the experiments bring out clearly the enormous difference between a solution and a supension.

The safe ground to take is: that the Brownian movements are due to the incessant bombardment by the molecules of the liquid; that the Brownian movements tend to make finely-divided, suspended particles distribute themselves throughout the liquid; that the uniform distribution is affected by the force of gravity, as in the case of a gas; and that the Brownian movements, though causing diffusion, give rise to no appreciable osmotic pressure. Very finely divided particles (less than 0.5 μ for instance) will be kept in suspension indefinitely by the Brownian movements, provided the particles remain finely divided. If enough particles agglomerate or coalesce, the force of gravity may cause the resulting masses to settle to the bottom of the containing vessel. We have therefore to consider some of the conditions under which particles coalesce or agglomerate.

COALESCENCE OF LIQUIDS.

If two small drops of a pure liquid are brought in contact, they run together and form a larger drop. The two small drops are therefore instable with respect to a larger drop. Consequently we should expect the small drops to distill over to, and condense on, a larger drop. This is equivalent to saying that the vapor pressure is higher the greater the curvature of the drop, a conclusion discussed by Lord Kelvin [123] many years ago. He considers that the theory, originally due to Laplace, is applicable to cases in which the radius of curvature is as small as 1.2 μ, but he thinks that we are not entitled to push it much further. Consequently he believes that the formulas given in his paper are not applicable to the vapor pressures of moistures retained by such substances as cotton cloth and oatmeal at temperatures far above the dew-point of the surrounding atmosphere, though the difference is quantitative and not qualitative. The rate at which small drops coalesce depends on the mobility of the liquid. With viscous liquids, such as cooling lavas or slags, one may get all sorts of phenomena which do not correspond to equilibrium relations.

COALESCENCE OF SOLIDS.

While it is perfectly familiar to everybody that two small drops of a pure liquid will coalesce readily to form a larger drop, all our ordinary experience is the other way in regard to solids, and yet, theoretically, finely divided solids behave like finely divided liquids in many respects. A very finely divided powder must have a higher vapor pressure, a lower melting-point, and a greater solubility [124] than the same substance in a more coarsely crystalline form. Crystals of iodine having a diameter of 2 to 3 mm. were kept in the dark for eight years. At the end of that time von Jonstorff [125] found that the smaller crystals had mostly disappeared, and that the crystals were now about 4.5 mm. in diameter. Pawlow [126] states that crystals of salol which were 2 μ in diameter melted 1.1° lower than crystals 40 μ in diameter. Comparing a fine dust of less than 2 μ diameter with crystals 0.5 to 2 mm. diameter, differences of 4° to 7° were obtained with

[123] *Phil. Mag.* (4), **42**, 448 (1871).
[124] Ostwald, *Zeit. phys. Chem.*, **35**, 495 (1900).
[125] *Ber. deutsch. chem. Ges.*, **10**, 866 (1877).
[126] *Zeit. phys. Chem.*, **65**, 1 (1908), **68**, 366 (1909).

salol, antipyrin, and phenacetin, but it seems probable that part of these differences is due to impurities and part also to experimental error.

Hulett [127] found practically no difference for the solubility of calcium sulphate in water until the diameter of the crystals was less than 4 μ. Changing from 4 μ to 0.6 μ caused an increase in solubility of nearly 20 per cent. A coarsely crystalline barium sulphate (3.6 μ) was soluble 2.3 mg. per liter. When ground in an agate mortar to 0.2 μ the solubility rose to 4.5 mg. per liter. The corresponding figures with natural barytes were 2.4 mg. and 6.2 mg. Red mercuric oxide has a solubility of 50 mg. per liter at 25°; when ground to a fine powder the color becomes yellow and the solubility increases to 150 mg. per liter.

The reason that the two parts of a broken plate do not coalesce when pressed together is that the film of condensed air acts as an elastic cushion and keeps the two parts from coming actually in contact.[128] If we heat the fragments of any broken object, less gas is adsorbed at the higher temperature and is held less firmly. If the solid becomes more malleable, it is easier to make contact at a number of points. It is possible to make two glass rods unite at temperatures at which the glass is still very viscous. It may be urged that glass at those temperatures is unquestionably a liquid and not a solid. This criticism does not apply to platinum, and it is easy to weld two pieces of platinum at temperatures far below that of the melting-point. In some cases two surfaces will unite fairly readily. This is very noticeable with unvulcanized rubber, from which it should follow that vulcanized rubber adsorbs air much more strongly. I do not know of any experiments along this line. While it is not possible, as a usual thing, to mend a broken object by pressing the two pieces together at ordinary temperatures, Spring [129] has shown that powders may be welded into massive blocks by the use of sufficiently high pressures. This means that the pressure has been sufficient to squeeze out the air films.

[127] *Ibid.*, **37**, 385 (1901); Jones and Partington, *Jour. Chem. Soc.*, **106**, II, 612 (1915).

[128] See Breuer, "Kitte und Klebstoffe," 23 (1907).

[129] *Bull. Acad. roy. belg.* (2), **49**, 323 (1880); *Ann. Chim. Phys.* (5), **22**, 170 (1881); *Ber. deutsch. chem. Ges.*, **15**, 395 (1882); *Bull. Soc. chim. Paris* (2), **40**, 520 (1883); Friedel, *Ibid.* (2), **39**, 626 (1883); **40**, 526 (1883); Jannetz, Neel and Clermont, *Ibid.* (2), **40**, 51 (1883); Tammann, *Zeit. Elektrochemie*, **15**, 447 (1909).

Since solids will coalesce when heated and subjected to pressure, there is no reason why some solid powders should not coalesce to some extent under the influence of gravity when heated. This is known as sintering or sometimes as fritting. The two terms are not distinguished as sharply as they might be.[130] Sintering should be used when a powder coalesces without melting or with but slight fusion, so that the product is still granular and more or less porous. Fritting should be used when the fusion is quite marked and the product is distinctly glassy. The formation of bricks and pottery involves sintering while the materials for glazes are fritted. There has been some question whether sintering can take place without incipient fusion,[131] but it is clear that a pure crystalline substance may sinter.[132] The brown gold obtained in assaying sinters to yellow gold when heated,[133] and I am told that the sintering of tungsten powder is done technically. Soot becomes sandy if heated too long or too hot. Many precipitates sinter on standing, though the change is not usually called that.

Other things being equal, the sintering is greater, and consequently the density, the higher the temperature. Bricks are less porous the higher the temperature of burning. Of course, if the temperature of vitrification is reached, a new phenomenon occurs. Magnesia is more dense the higher it is heated,[134] and so is lime.[135] The agglomeration is often accompanied by increased resistance to chemical action. Strongly heated lime reacts very slowly with carbon dioxide.[136] After short ignition, silica dissolves in a boiling solution of potassium or sodium carbonate; after long ignition it does not.[137] The apparent action of caustic

[130] Percy's Metallurgy: "Fuel," 46, 280 (1875).

[131] Lucas, *Zeit. phys. Chem.*, **52**, 327 (1905); Endell, *Silikat-Zeitschrift*, **2**, 1, 25 (1914); Kohlschütter, *Liebig's Ann.*, **398**, 37 (1913).

[132] Cf. Day and Allen, Carnegie Inst. Pub. **31**, 59 (1905); *Zeit. phys. Chem.*, **54**, 39 (1906).

[133] Percy's Metallurgy: "Silver and Gold," 268 (1880); Hanriot, *Comptes rendus*, **151**, 1355 (1910); **152**, 216 (1911).

[134] Ditte, *Comptes rendus*, **73**, 270 (1861); Moissan, *Ibid.*, **118**, 506 (1891).

[135] Wright, *Zeit. anorg. Chem.*, **68**, 397 (1910).

[136] Raoult, *Comptes rendus*, **92**, 189 (1881); Sosman, Hostetter and Merwin, *Jour. Wash. Acad. Sci.*, **5**, 563 (1915).

[137] Rammelsberg, *Jour. Chem. Soc.*, **26**, 242 (1873); cf. Laufer, *Ber. deutsch. chem. Ges.*, **11**, 60, 935 (1878).

alkali on hydroxides and of gelatine and ammonia or potassium bromide on silver bromide is decreased enormously if the precipitates are allowed to stand over night.

PLASTICITY.

A plastic substance is one which can be moulded by pressure.[138] This connotes that any break due to deformation is self-healing. A mobile liquid is not plastic, because it will not retain its shape. With increasing viscosity a liquid becomes plastic. Molasses candy is plastic until it crystallizes. Semifused glass is plastic. The time factor may be important. Sealing-wax is brittle if the pressure is applied rapidly, but is plastic if the rate of deformation is low. Since metals and other solids coalesce under high pressure, there is no reason why they should not be plastic under similar conditions, as indeed they are. We make use of this property when squirting metals into rods or pipes. Under high pressure ice is plastic. It has been claimed by Spring[139] and by Kahlbaum[140] that solids become almost like mobile fluids under high pressure, but it seems to have been proved conclusively by Spezia[141] that this is not true when the pressure is uniform, and that the apparent fluidity occurs only when there is a shearing force. Iron filings in presence of a magnet might be considered a special case of plasticity, though not one of any great interest. Another special case of partial plasticity is the mineral itacolumite,[142] which is said to have a structure akin to a series of ball-and-socket joints.

Between the extreme cases of a solid such as a metal and a liquid such as glass or molasses candy we have the intermediate case of putty, which is whiting and oil, or a solid with a liquid film around it. If a liquid is adsorbed strongly by a solid, the thin film will hold the solid particles together, while still permitting them to move relatively to one another. A liquid film may therefore act as a bond for solids and may make the mass plastic. Oil is used as a binder in roads and to make plastic putty. Everybody knows that dry sand cannot be moulded,

[138] Duff, "A Text-Book of Physics," 119 (1916).
[139] *Bull. Acad. roy. belg.* (2), **49**, 364 (1880).
[140] *Verh. Naturforscher ges. Basel*, **15**, 14 (1903).
[141] *Atti Acad. Sci. Torino*, **45**, 525 (1911); **46**, 682 (1912).
[142] Wetherill, *Chem. News*, **22**, 266 (1870).

whereas wet sand can. Plastic dynamite is made by adding three parts of nitroglycerin [143] to one part of diatomaceous earth. Bingham [144] has made a preliminary study of the concentration at which plasticity begins or ends. If a finely powdered solid is added to a liquid, the viscosity of the liquid is increased or the fluidity, which is the reciprocal of the viscosity, is decreased. Over the range from 25° to 60° the concentration for zero fluidity was independent of the temperature. With infusorial earth in water, zero fluidity was reached at a volume concentration of about 87 per cent: water; with China clay at about 96 per cent.; with the graphite used in Acheson's aquadag at about 94.5 per cent., and with an unspecified clay at about 80.5 per cent. With infusorial earth in alcohol, zero fluidity was reached at a volume concentration of about 88 per cent. alcohol. The mixtures having zero fluidity are not stiff and will not hold their shape. At higher concentrations of the solid there is a change from viscous flow to plastic flow. The distinction made by Bingham is that with viscous flow any shearing force—no matter how small—will produce permanent deformation, whereas, in the case of plastic flow, it is necessary to use a shearing force of finite magnitude in order to produce a permanent deformation. It seems reasonable to assume that zero fluidity corresponds to the point when liquid enough is present just to scatter the particles; in other words, when about enough liquid is added to fill the voids. This was true in the one case studied by Bingham. The clay referred to contained 81.6 per cent. voids and required 80.5 volume per cent. of water to bring it to zero fluidity. Of course, this very important generalization of Bingham's must be tested in more cases before it can be considered as definitely true, but it is so obvious, after it has been pointed out, that it cannot be far wrong. Bingham's law, if we may so call it, may be of distinct importance in the paint industry. The oil requirement for a given pigment is a very arbitrary amount, and experts often differ widely in their values. Reproducible figures could be obtained if in each case there was determined the amount of oil necessary to give zero fluidity.

The clay-workers use the word plasticity in a special sense to denote that a clay is plastic and will burn to a coherent mass. From

[143] Thorp, "Outlines of Industrial Chemistry," 482 (1916).

[144] *Am. Chem. Jour.*, **46**, 278 (1911); JOUR. FRANKLIN INST., **181**, 845 (1916).

this point of view a mass of wet sand is not plastic, because it falls to pieces when dried. To satisfy this new definition we must have in the water some bonding material, presumably in a gelatinous form. There is no difficulty in accounting for a gelatinous film.[145] Cushman[146] has shown that the cementing power of rock powders is due to the formation of gelatinous silica, ferric oxide, etc. If we have a gelatinous material which is adsorbed strongly by the solid particles and which can take up and lose water, we shall have plasticity. In the case of clay the gelatinous material may be hydrous alumina, hydrous silica, or some intermediate composition. The difficulty, however, is to account for its remaining plastic after moderate drying, to account for its re-adsorbing water to form a gelatinous mass. This is probably due to the presence of some salt, but we do not know what salt, and consequently we cannot tell why one clay is plastic and another not, and we do not know what we should add to a non-plastic clay to make it plastic. The whole thing is probably very simple, but no one has yet attacked it in a rational way.

Summary.

In this paper there has been given a discussion of: adsorption from solution by solid; the adsorption isotherm; abnormal adsorption; negative adsorption; reversibility of equilibrium; specificity of adsorption; adsorption of several solutes; adsorption from solution by liquid; adsorption and surface tension; Brownian movements; coalescence of liquids; coalescence of solids; plasticity.

CORNELL UNIVERSITY.

[145] Quincke, *Drude's Ann.*, **7**, 74 (1902).
[146] *Jour. Am. Chem. Soc.*, **25**, 451 (1903).

THE SPECTRAL SELECTIVITY OF PHOTOGRAPHIC DEPOSITS.*

Part I. Theory, Nomenclature, and Methods.

BY

L. A. JONES and R. B. WILSEY.

IT is well known among practical photographers that the color of the silver deposit in a photographic negative exerts a marked influence upon the quality of the resulting print. Thus negatives made with certain developers exhibit decidedly yellowish deposits, while other developers produce images that are entirely colorless. Of two such negatives having the same visual quality except for the differences in color, the yellowish one will produce a print of decidedly greater contrast. The reason for this is immediately apparent upon consideration of the difference between the visibility function of the eye and the spectral sensibility (analogous to the visibility function) of the photographic printing material. The maximum of the visibility function lies at 554$\mu\mu$ in the green region of the spectrum, while the maximum of the photographic spectral sensibility is located in the violet between 380$\mu\mu$ and 440$\mu\mu$, the exact location varying between these limits for different sensitive materials. A deposit which is yellowish—that is, having excessive absorption for radiation of the shorter wave-lengths—therefore, will have a lower total transmission when measured by using some photographic material as a receiving surface for the transmitted radiation than when measured by a visual method in which the retina of the eye is employed as the light-sensitive receptor.

It is evident, then, in a study of negative quality, from the standpoint of tone reproduction, that a careful distinction must be made between the visual total transmission and the photographic total transmission of the silver deposits which compose the negative. Since the conception of photographic total transmission as distinguished from visual total transmission of such

* Communicated by Dr. C. E. K. Mees. Communication No. 57 from the Research Laboratory of the Eastman Kodak Company.

deposits is more or less new, it seems desirable, for the sake of clearness and uniformity in the terminology of future work to be done along this line, to define and name certain of the terms involved, and to outline experimental methods for their measurement.

In view of the fact that this paper is to deal with the relations existing between certain sensitometric constants as measured by two different methods, the visual and photographic, it may be well to review briefly the general methods in use at present in photographic sensitometry. These methods are based in general upon the work of Hurter and Driffield [1]; and to the papers published by them and the later photographic literature the reader is referred for detailed information regarding the theory, methods, and apparatus involved.

In order to obtain the characteristic curve of a photographic material (usually called the H. & D. curve) it is necessary to subject various areas of that material to series of known exposures varying over a wide range of magnitude. The exposed material is then developed, fixed, washed, and dried according to a set of standardized conditions, after which the extent of blackening produced by each of the different exposures is determined by some visual photometric method. The series of exposures, for the sake of convenience in plotting the results, usually vary according to some logarithmic function, such as by successive powers of 2 or of $\sqrt{2}$, and are given by a sensitometer embodying either some form of rotating sector wheel or some type of moving plate. The latter method is superior to the rotating wheel, as thus the errors due to intermittency, which are large under certain conditions, are entirely eliminated. The measurement of the total transmission of the various blackened areas may be made by any one of several types of photometer, the chief requirement being that the values obtained shall be the diffuse transmissions of the deposits measured. This result is usually obtained by placing the deposit, while being measured, in contact with a sheet of ground pot opal glass. The data thus obtained consist of a series of diffuse transmission values corresponding to a series of known exposures. Experience has shown that these data are most easily interpreted if plotted as a curve having log exposures as abscissæ

[1] Hurter and Driffield, *Journal of Society of Chemical Industry*, 1890.

and density values as ordinates, the density values being derived from the transmission values by the relation,

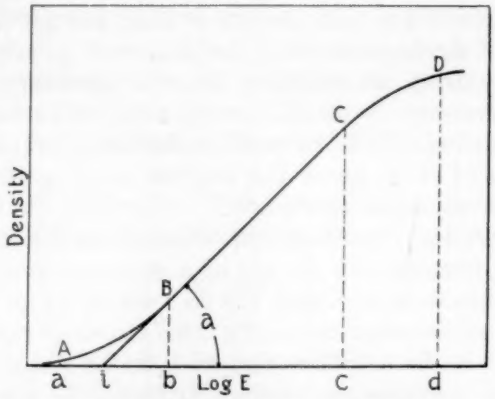
$$\text{Density } (D) = \log \frac{1}{\text{Transmission}} = \log \text{opacity},$$

$$D = \log \frac{1}{T} = \log O.$$

Such a curve is shown in Fig. 1.

It will be found that a portion of such a curve approximates closely to a straight line, the projection of which upon the x axis gives the "Latitude" value for that photographic material. The length of the straight line portion varies greatly with various types of photographic materials. In some cases the straight line may be entirely absent, being reduced to a point of inflection, while

FIG. 1.



in the best negative materials the value of latitude (expressed in exposure units) may be as high as 250 or even 500.

The numerical values usually read from such curves (Fig. 1) and taken as representative of the characteristics of the material, are:

$$\text{Gamma } (\gamma) = \tan a$$
$$\text{Latitude } (L) = \log E_c - \log E_b$$
$$\text{Total Scale } (T) = \log E_d - \log E_a$$
$$\text{Speed } (S) = \frac{k}{i}$$

Where "a" is the angle between the straight line portion and the x axis, "k" is a constant depending upon exposure conditions, and "i" (inertia) is the value of E (exposure) where the straight line extended cuts the x axis. The positions of the points A and D (limits of the useful scale of the material) are established

arbitrarily at the points on the curve where $\frac{dD}{d \log E} = 0.2$, it being considered that any portion of the curve having a gradient less than this value is practically useless in the reproduction of tone differences.

It is evident that, since the constants of a material determined in this way are dependent upon the total transmission values of the various silver deposits measured by some visual photometric method, such constants, when used for computing the effect of printing a negative upon a positive material, are correct in general only when applied to a positive sensitive surface having a spectral sensibility function identical with the visibility function of the retina. Since in all problems of tone reproduction we are interested in the effect of the negative on the positive material (which may be carried either upon an opaque base, such as paper, or upon a transparent medium, such as glass or film) and not in the visual appearance of the negative itself, and since such positive materials differ greatly from the retina in spectral sensibility, it follows that it is necessary to determine the total transmission values of the various deposits as referred to the sensitive positive material being used or to know the relation existing between such values and those measured visually.

The theoretical considerations involved in this problem are most clearly presented by the aid of a graphic representation of the various functions necessary for its solution (Fig. 2). Let us make the initial assumption that the same source of radiant energy is to be used in the determination of both the visual and photographic total transmission values. It should be borne in mind that this assumption applies to all discussion presented in this paper.

The various functions necessary for the complete mathematical solution of the problem are:

$J = f(\lambda)$ = Spectral energy distribution of the illuminant used for the measurement of both the visual and photographic values.

$T = f(\lambda)$ = Spectral transmission function of the deposit for which the visual and photographic total transmission values are desired.

$V = f(\lambda)$ = Visibility function of the retina.

$S = f(\lambda)$ = Spectral distribution of sensibility for the photographic surface.

$B = f(\lambda)$ = Spectral transmission function of the material (glass, film, etc.) upon which the silver deposit to be measured is supported.

The symbols J_λ, T_λ, V_λ, S_λ, and B_λ, are used to designate the values of these various functions at some particular wave-length, λ. The ordinate values of the J function are in terms of relative energy; those of the T and B functions are the ratio of the transmitted to the incident radiation (pure numerics); while those of the V function are relative brightnesses of an equal energy source, plotted with maximum ordinate equal to unity. The ordinates of the sensibility function, S, represent relative sensitiveness, plotted with maximum ordinate equal to unity.

Although from a physical standpoint these spectrophotometric curves represent a complete specification of the characteristics of the various elements, they do not furnish the desired values in a directly usable form. For instance, in case of the spectral transmission function, T, of the silver deposit the thing of interest from the standpoint of tone reproduction is not its transmission at any particular wave-length, but the total transmission of that deposit as measured either by the retina or by the photographic material as a receiving surface. The functions shown in Fig. 2 do, however, provide the data from which the desired values may be computed.

For the determination of the visual total transmission, T_v, the following relations are found to exist:

$$\int_0^\infty J_\lambda V_\lambda \, d\lambda = E \cdot c$$

and

$$\int_0^\infty J_\lambda V_\lambda T_\lambda \, d\lambda = E' \cdot c$$

where E = Total incident luminous flux.
E' = Total transmitted luminous flux.
c = constant of proportionality.

$$T_v = \frac{E'}{E} = \frac{\int_0^\infty J_\lambda V_\lambda T_\lambda \, d\lambda}{\int_0^\infty J_\lambda V_\lambda \, d\lambda}.$$

Similarly for the photographic total transmission, T_p,

$$\int_0^\infty J_\lambda S_\lambda B_\lambda \, d\lambda = A \cdot c'$$

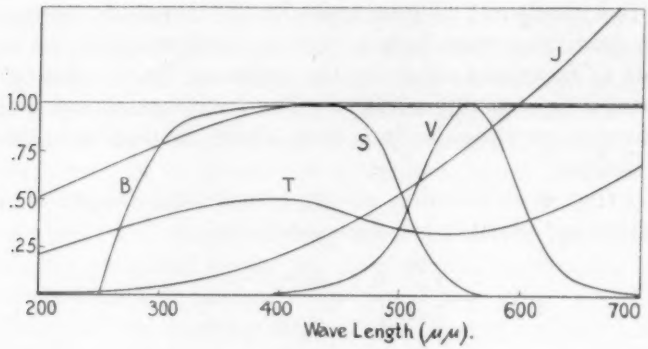
$$\int_0^\infty J_\lambda S_\lambda B_\lambda T_\lambda \, d\lambda = A' \cdot c'$$

where A = Total incident actinic flux.
A' = Total transmitted actinic flux.
c' = constant of proportionality.

$$T_p = \frac{A'}{A} = \frac{\int_0^\infty J_\lambda S_\lambda B_\lambda T_\lambda \, d\lambda}{\int_0^\infty J_\lambda S_\lambda B_\lambda \, d\lambda}$$

A complete and precise knowledge of the five functions shown in Fig. 2, therefore, would enable one to compute both the visual and photographic total transmission values for any given deposit. However, at present, certain of these functions are not known with sufficient precision, and their determination presents so many practical difficulties that it is more feasible to adopt some more direct method for the measurement of the values desired. The foregoing theoretical considerations have been presented not so much for their value in practical work but rather to assist in arriving at a clear understanding of the various factors upon which the values of visual and photographic transmission depend. Work is in progress at present on the improvement of apparatus

FIG. 2.



and methods used in measurement of these uncertain factors, and it is hoped that sufficient precision will be secured to make the above method useful in checking the values of total transmission obtained by direct measurement.

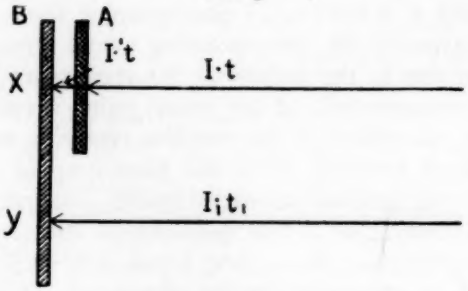
Now, turning to the direct methods of measuring these values, little need be said concerning the visual methods, since these are generally well understood. As previously stated, the value desired from the photographic standpoint, at least in all cases where a positive is to be made by contact printing from the negative, is that of "diffuse" density. The deposit to be measured, therefore, is illuminated by perfectly diffused light of the specified quality and E and E', the incident and transmitted intensities, are measured.

Then,

$$T_v = \frac{E'}{E}.$$

In making such measurements the retina is used as the sensitive receiving surface, and, since retinal response, at the intensities ordinarily used in such work, is proportional to the rate at which radiant energy impinges upon it, the measurement of visual transmission is independent of the time factor. The response of a photographic material, however, is not independent of time, being a function of both the intensity and the time of exposure. Over a considerable range of intensity values the response is proportional to the product of intensity by time ($I \cdot t$), but this law breaks down for low values of intensity. This failure of the

FIG. 3.



reciprocity law, as it is called, complicates to a certain extent the definition of the term photographic total transmission. In order to make the definition of this term, T_p, strictly analogous to that of visual transmission, T_v, and also to eliminate any effect of the failure of the reciprocity law, the following method is employed:

In Fig. 3, let A represent a photographic deposit the transmission of which is to be measured, and B the photographic sensitive surface for which the value of total transmission of A is desired. Let an exposure $I \cdot t$ be incident upon A. The area x of B which is covered by A thus will receive an exposure $I' t$, the value of which will depend upon the photographic total transmission of A.

Let an exposure $I_1 \cdot t_1$ be incident upon the area y of B, a portion of B not covered by A.

Now let the two areas x and y be developed to the same extent, *i.e.*, $\gamma_x = \gamma_y$, thus producing the densities D_x and D_y.

If $D_x = D_y$

and $t = t_1$

it is evident that $I' = I_1$.

$I \cdot t$ = Exposure incident upon A.

$I' \cdot t$ = Exposure transmitted by A.

Therefore,

$$T_p \text{ (for } A) = \frac{I' \cdot t}{I \cdot t} = \frac{I'}{I} = \frac{I_1}{I}.$$

And since

$$D = \log \frac{1}{T},$$

$$D_p \text{ (for } A) = \log \frac{1}{T_p} \text{ (for } A)$$

$$= \log \frac{I}{I_1}.$$

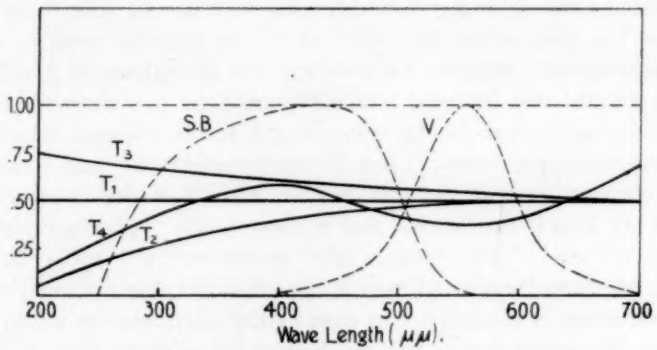
In this way a definition of photographic total transmission strictly analogous to the corresponding visual term is obtained, and any error due to the failure of the reciprocity law is eliminated. The measurement of the visual value is made by a null method, using the retina as the sensitive receiving surface, while by the definition outlined above the photographic value is also obtained by a null method, but by using the photographic material as the sensitive receptor. The requirement that $D_y = D_x$ in the discussion above makes the method a null one, while the assumption that $t = t_1$ is necessary for the elimination of errors due to reciprocity failure. It should be borne in mind that the value of photographic total transmission of any deposit depends upon the spectral sensibility of the material by which it is measured, and hence such values are correct only for materials having the same spectral distribution of sensibility. Photographic materials differ greatly in this respect, some being sensitive only to the extreme violet and ultra-violet while others respond to the entire visible spectrum as well. However, the great majority of positive materials available at present are quite similar in regard to spectral sensibility and measurements show that although differences do exist they are not of sufficient magnitude to cause serious errors in the results when using the value of photographic total transmission obtained by one material for work with others. These remarks apply only to the group of most extensively used developing-out papers and positive plates and films. A large amount of data has been obtained on this subject, and will be

presented in the later parts of this paper, dealing with the more practical phases of the subject.

Now let us consider briefly the effect of the various forms of the transmission function upon the photographic and visual values of total transmission, and upon the relations existing between these values. In Fig. 4 are shown a few possible forms of this function.

The visibility, sensibility, and base transmission functions are shown as dotted curves, while the hypothetical T functions are shown as full lines and designated by number. No. 1—The value of T_λ is constant for all values of λ. Such a deposit is colorless (*i.e.*, neutral), and for such deposits $T_v = T_p$. No. 2.—The value of T_λ increases with increasing wave-length. Visually such de-

FIG. 4.



posits appear yellowish in color and $T_v > T_p$. This case represents practically all photographic images obtained by development with pyrogallic acid developers, the exact shape of the function depending upon the constitution of the developing solution, nature of fixing bath, etc. No. 3—The values of T_λ decrease with increasing wave-length. Such a deposit appears bluish in color and $T_v < T_p$. It is possible to obtain such deposits by use of indoxyl as the developing agent and also by some amidol formulæ.

From an inspection of the positions and shapes of the S and V functions, Fig. 4, it is apparent that it is possible to have deposits that may be entirely colorless (*i.e.*, non-selective throughout the visible spectrum) but with values of T_v either greater or less than those of T_p. The contrary may also be true; that is, a colored

deposit for which $T_v = T_p$. An example of such a case is given by a silver deposit which has been intensified by a copper-tin method.[2] Visually this deposit has a magenta color and actual measurements gave $T_v = T_p$. A hypothetical curve representing this case is shown as No. 4, Fig. 4. By means of developing solutions so constituted as to control the state of division in which the silver is deposited it is possible to cause a great variation in the shape of the transmission function of the silver image and hence to alter the ratio of photographic to visual transmission. A wide variation in this factor also occurs in the case of many intensified deposits, especially in those cases where intensification is produced by the addition of materials other than silver to the original silver deposit.

Certain terms are frequently applied as descriptive of the transmission function of transmitting media, and in order to avoid confusion their meaning should be clearly defined. The term "selective" is used when the value of T_λ is variable with λ, while "non-selective" implies T_λ constant for all values of λ. These terms should not be used unaccompanied by a statement, either verbal or numerical, of the wave-length limits between which the implied condition exists. Thus "visually selective" and "visually non-selective" apply only to visible radiation the approximate limits of which are 400$\mu\mu$ and 700$\mu\mu$; while "photographically selective" and "photographically non-selective" apply to that range of wave-lengths to which the photographic material under consideration is sensitive. In case of the particular problem with which this paper deals, the production of a print from a series of silver deposits of varying density supported on a glass plate or film, the effective limits are approximately 500$\mu\mu$ and 280$\mu\mu$, the latter limit being determined by the base on which the deposit is supported (glass or film). The term colored as applied to a transmitting medium is analogous to "visually selective," while "neutral" has the same meaning as "visually non-selective." These terms may be summarized as follows:

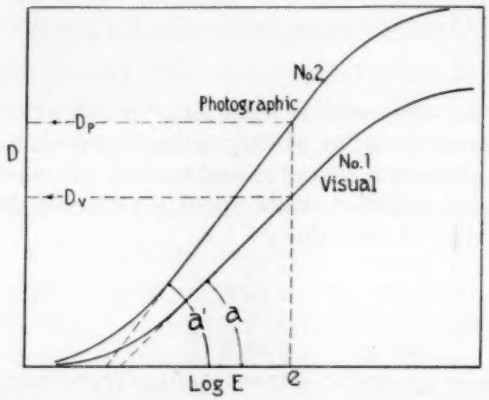
$T_\lambda = K$ (between 400$\mu\mu$ and 700$\mu\mu$)—Visually non-selective or neutral.
$T_\lambda \neq K$ (between 400$\mu\mu$ and 700$\mu\mu$)—Visually selective or colored.
$T_\lambda = K$ (between 280$\mu\mu$ and 500$\mu\mu$)—Photographically non-selective.
$T_\lambda \neq K$ (between 280$\mu\mu$ and 500$\mu\mu$)—Photographically selective.

[2] Nietz and Huse, "The Sensitometry of Intensification." To appear in a future issue of this JOURNAL.

Thus far the discussion has dealt only with the relative visual and photographic densities of a single silver deposit. Now let us turn to a consideration of the effect upon the characteristic curve of a photographic material resulting from the use of transmission (or density) values determined photographically rather than visually.

Considering a series of deposits, varying over a wide range of density, produced by any specified photographic method, we cannot in general assume that the ratio of T_p/T_v will be constant for the entire series. Hence both the shape and position of the curve may be changed by the use of the photographic values, and thus all of the sensitometric constants may be altered in value. Obviously, the constants obtained from the photographic values

FIG. 5.



are the ones of greatest importance, for, since the negative is only an intermediate step in the process of reproduction, the visual appearance of the negative is of relatively little importance.

In Fig. 5 are shown the two curves illustrating a possible relation between the visual and photographic characteristics of a photographic plate.

Curve No. 1 is plotted from the visual density values and No. 2 from the photographic values of the same deposits. Now for any value of exposure, e, the corresponding values of D_v (viusal density) and D_p (photographic density) can be determined. Also both visual and photographic values of gamma, γ_v and γ_p, can be computed.

$\tan a = \gamma_v$ = Visual gamma.
$\tan a' = \gamma_p$ = Photographic gamma.

Likewise photographic values of all the various sensitometric constants, such as gradient, latitude, scale, inertia, etc., can be obtained.

The ratio between the visual and photographic values of certain of these constants is of considerable usefulness in expressing numerically the characteristics of negatives made by various processes, and hence it seems desirable to apply distinguishing terms to them.

For any value of exposure, e, Fig. 5:

$$\frac{D_p}{D_v} = \text{Selectivity coefficient of density} = \triangle \text{ (Delta)}$$

$$\frac{d\,D_v}{d\log E} = \text{Visual gradient} = G_v$$

$$\frac{d\,D_p}{d\log E} = \text{Photographic gradient} = G_p$$

$$\frac{\dfrac{d\,D_p}{d\log E}}{\dfrac{d\,D_v}{d\log E}} = \text{Selectivity coefficient of gradient} = \phi \text{ (Phi)}$$

These terms apply only to some single value of exposure, and such values are descriptive of only a single deposit or of a single point on the characteristic curve and are not of use in specifying the quality of a negative made up of a series of different densities. However, if the value of

$$\frac{\dfrac{d\,D_p}{d\log E}}{\dfrac{d\,D_v}{d\log E}}$$

is constant over the entire exposure range represented in a negative, this ratio may be taken as representing the selective character of that negative. Since the contrast of a negative is some function of the gradient, we may consider the value of the above ratio as an expression of the ratio of the photographic to the visual contrast, and hence for any negative for which this ratio is constant for all values of exposure this term may be called the "selectivity coefficient of contrast," K (Kappa), of the negative.

Still another special case of the general problem is for the condition (in addition to the last limitation that the selectivity coefficient of gradient is constant) that the terms $\frac{d\,D_p}{d\log E}$ and $\frac{d\,D_v}{d\log E}$ are each constant for a considerable range of exposure. This condition exists over the straight-line portion of the curve,

and the projection of this portion of the curve on the x axis gives the value of latitude for that sensitive material.

Under these conditions.

$$\frac{\gamma_p}{\gamma_v} = \frac{\dfrac{d\,D_p}{d\log E}}{\dfrac{d\,D_v}{d\log E}} = \text{color coefficient} = \chi \text{ (Chi)}.$$

In order to be strictly consistent in nomenclature, this term, $\frac{\gamma_p}{\gamma_v}$, should be called the selectivity coefficient of gamma, but since it must be used so frequently it is proposed to sacrifice precision of terminology for the sake of utility and to shorten the term to "color coefficient."

The word "color" used in this way is more or less misleading, for a negative showing no color (visually non-selective) may still be photographically selective and hence have a value of $\frac{\gamma_p}{\gamma_v}$ (color coefficient) other than unity, but for lack of a better term "color coefficient" has been adopted as being most convenient for use. The "color coefficient" is in practice the most useful constant for expressing the relation existing between its visual and photographic characteristics. For, as was previously pointed out, a straight-line portion ($\frac{d\,D}{d\,\text{Log}\,E}$ = constant) is found in the characteristic curve of the majority of sensitive materials, and in a good negative material the length of this line is sufficiently great so that all ordinary subjects may be rendered on that portion of the curve. A good negative material should have a latitude of not less than 75, and, since but a very small percentage of subjects to be photographed have a contrast greater than 1 to 75, it is evident that by proper exposure the entire range of tones can be placed upon the straight-line portion of the curve and then, by developing to the proper extent, an exact reproduction of tone can be obtained in the negative. Under such conditions contrast is directly proportional to gamma, and the values "selectivity coefficient of contrast" and "color coefficient" become identical.

Having discussed the various relations existing between the visual and photographic characteristics of a negative, we come now to the consideration of the methods involved in the measurement of these relations in practice. The method used for the de-

termination of the photographic transmission of a deposit must give values in conformity with the requirements of the definition of that term as outlined previously in this paper, involving the use of a null method free from errors due to the failure of the reciprocity law. Having determined D_p for each area of a sensitometric strip, a curve can be plotted with these D_p values against log E. In this way curve No. 2, Fig. 5, is obtained, and having this, together with the visual curve, No. 1, the various constants, such as color coefficient, etc., can be computed. The measurement of the photographic density of a series of deposits, in strict conformity with the definition of that term, may in some cases be unnecessary or even undesirable from the practical standpoint. However, as such values are sometimes desired, methods for obtaining such values will be outlined. Two such methods are presented, the first being as general and complete a solution of the problem as is possible in the light of our present knowledge of the subject, while the second is shorter and applicable only under certain conditions.

I. General Method for D_p.

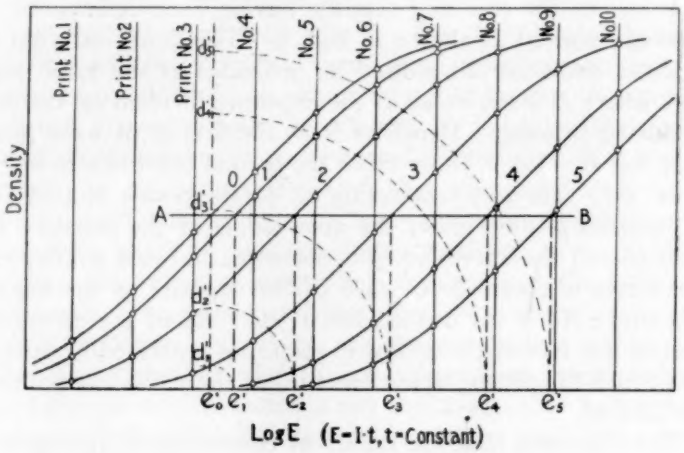
This method involves the making of several prints from the sensitometric strip made up of the various densities to be measured, these prints being made with the strip in contact with the photographic material to which the values of D_p are to be applied. Successive prints differ in that the intensity factor, I_t, of the exposure incident upon the negative strip in printing is varied from print to print in some known manner, while the time factor, t_t, is kept constant for all prints. All of these prints are then developed to exactly the same extent, fixed, washed, dried, and the densities of the resulting deposits measured visually in the usual way. In case the positive material is coated on a transparent base the density values are read by transmitted light and $D = \log \frac{I}{T}$. If, however, the positive material is coated on an opaque support, such as paper, the density readings are obtained by reflected light, density being defined in this case by the equation $D = \log \frac{I}{R}$ where R is the reflecting power of the deposit as measured under specified conditions regarding the angle of illumination and observation.[3] From this set of prints a series of

[3] Jones, Nutting and Mees, *Phot. Jour.*, December, 1914, p. 342.

incident intensity values, all of which produce the same density in the prints, are obtained which are inversely proportional to the photographic total transmissions of the various deposits composing the negative strip. The procedure in obtaining the results can best be explained by a graphic presentation of the data as shown in Fig. 6.

Assume that the negative strip consists of six areas, 0, 1, 2, 3, 4 and 5, the visual density values of which are d_0, d_1, d_2, d_3, d_4, and d_5, and the photographic density values d_0, d'_1, d'_2, d'_3, d'_4, and d'_5. The series of prints are made from this strip on the positive

FIG. 6.



material for which it is desired to determine the values of d'_1, d'_2, etc. Let E_i be used as a general symbol for the exposure incident upon the negative, and E_t for the exposure transmitted by the negative.

$$E_i = I_i \cdot t_i \text{ and } E_t = I_t \cdot t_t.$$

E_t, the transmitted exposure, is equal to the exposure incident upon the positive material at that point, $E'_i = (I'_i \cdot t'_i)$. E_i is increased in some known manner from print to print, usually by equal logarithmic increments, the magnitude of the increment from print to print being determined by the densities to be measured and by the character of the positive material being used.

Thus:

E_i for first print $= e = I_1 \cdot t_1$.
E_i for second print $= 2e = 2I_1 \cdot t_1$.
E_i for third print $= 4e = 4I_1 \cdot t_1$.
E_i for fourth print $= 8e = 8I_1 \cdot t_1$, etc.

The change in E_i must be accomplished by a variation of I_i, keeping t_i constant. Further, E_i should be varied over such a range that for its lowest value a low density is obtained on the positive material for the area of the negative where $D = 0$, while for the highest value of E_i a high density is obtained under the negative area having the highest density (d_5 in this case). The prints having been developed as previously specified and the density values of the resulting deposits having been determined, the values are plotted as shown in Fig. 6. The densities from any particular print are all plotted as ordinates at the same log E value, where E is the value of the exposure incident on the negative during printing. Densities from the first print were plotted where log E = log e, those from the second print where log E = log $2e$, etc. Then by connecting all of the points plotted from the densities printed under the area No. 0 of the negative (for which $D = 0$) the curve No. 0 is obtained, and in a similar manner a curve is obtained for each of the deposits on the negative strip, curve No. 1 for deposit No. 1, etc. All of the curves thus obtained will be exactly similar in shape but separated by intervals from which the photographic densities of the various deposits can be computed.

The statement that the family of curves shown in Fig. 6 are similar in shape (all curves having the same gradient at any particular value of D) depends on an assumption that should be mentioned at this point. Since the silver deposits being measured may be selective in transmission, it follows that the quality of the transmitted radiation may be different for the deposits of different density and also different from the quality of the incident radiation, which obviously is identical in quality with the radiation transmitted by the area of zero density; *i.e.*, directly incident upon the positive material. It is known that with some positive materials, at least, the gradient obtained with fixed conditions of development may vary with the wave length of the radiation used in making the exposure. It follows, therefore, if all the prints referred to above are developed for equal times, that

the change in the quality of radiation due to the selectivity of the negative deposits may result in different gradient values for the curves in Fig. 6. If such is the case, each negative density must be taken separately and a series of prints made from each, with I_i variable and t_i constant. The series of prints from each density are then developed together, the development time from series to series being so changed that the curves when plotted will all have the same gradient. In this way a set of curves similar to those shown in Fig. 6 will be obtained. In case it is found necessary to use various times of development in order to obtain curves having equal gradient, a developing solution must be used which produces no change of inertia with time of development; that is, one containing no bromide or only a very small amount. If the positive material being used contains free bromide, a change in the inertia will occur with a variation in development time, but this may be considered as a characteristic of the positive material and hence may rightfully be allowed to influence the density value of any given deposit as measured by that particular positive material. In practice it is found that the great majority of selective deposits obtained by ordinary processes of development change the quality of the transmitted radiation to so slight an extent that the variation in gradient obtained with fixed times of development is negligible and therefore the method outlined in Fig. 6 is applicable. However, the assumption that a fixed time of development will give curves of equal gradient should be borne in mind and its validity tested in any doubtful cases. It is evident that the methods outlined in this paper may be used in the determination of the photographic transmission of any transmitting medium, such as gelatine filters, colored glass, etc., as well as for silver deposits, such as make up negative images. In the case of highly colored media the variation of gradient with the quality of transmitted radiation may be quite appreciable, and in such cases the above assumption does not hold, and means must be adopted for obtaining curves of equal gradient without changing the inertia except in so far as the inertia is a function of gradient due to inherent characteristics of the positive material being used.

Returning now to a consideration of the curves as shown in Fig. 6, it is evident, upon examination, that curve No. 0 (for the negative deposit where $D = 0$) may be regarded as a true char-

acteristic curve of the positive material obtained by giving a series of exposures in which t_i is kept constant and I_i varied. By definition photographic transmission, T_p, is given by the ratio,

$$\frac{E_i}{E_t} = \frac{I_i \cdot t_i}{I_t \cdot t_i} = \frac{I_i}{I_t} = T_p,$$

where E_i = incident exposure,

E_t = transmitted exposure,

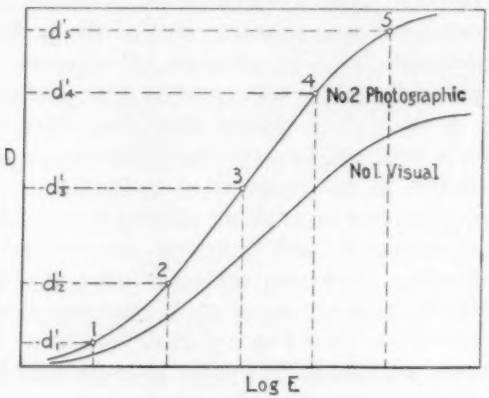
and $t_i = t_t$.

Therefore $$D_p = \log \frac{E_i}{E_t}$$

$$= \log E_i - \log E_t.$$

Now, if a line, AB, of constant density (any horizontal line) be drawn intersecting the curves 0, 1, 2, etc., and the log E values

FIG. 7.



of the points of intersection be read from the log E scale, D_p can be computed for the various negative deposits, 1, 2, 3, etc. Considering deposit No. 1, for instance, it is evident that an incident exposure e'_1, produces a density on the positive material equal to that produced by the exposure e'_0 incident through zero density, t_1 being equal to t_0. e'_0, therefore, must be equal to the exposure transmitted by the deposit No. 1. Hence,

$$D_p \text{ (for deposit No. 1)} = \log e'_1 - \log e'_0$$

and

$$D_p \text{ (for deposit No. 2)} = \log e'_2 - \log, e'_0, \text{ etc.}$$

The difference between log e'_0 and the log e' value for any other deposit, then, is equal to D_p for that deposit. Now in Fig 7

plot these values, making $d'_1 = \log e'_1 - \log e'_0$, $d'_2 = \log e'_2 - \log e'_0$, etc., against the log exposures given to the negative. These points, 1, 2, 3, 4, etc., give curve No. 2, which is the photographic characteristic of the negative referred to the positive material used, curve No. 1 being the visual curve of the same negative. It is evident that the d'_1, d'_2, etc., points can be established by a graphic method if desired by simply rotating the e'_1, e'_2, etc., points about e'_0 (Fig. 6) until they lie upon a perpendicular through e'_0, this perpendicular being the density scale with e'_0 at the point $D = 0$.

II. Shorter Method for D_p.

Referring again to Fig. 6, since all of the curves are of the same shape, it follows that the line AB may be drawn at any value of D without changing the value of $\log e'_1 - \log e'_0$ or D_p for deposit No. 1. It follows, furthermore, that the line the length of which determines the value of D_{p_1} need not be drawn at the same value of D as that which determined the value of D_{p_2} or of any other of the various deposits. Therefore if curve No. 0 be completely determined it is evident that only one point on each of the other curves is necessary for the solution of the problem. A single print from the negative strip (if E_i be of the proper magnitude) gives one point on each of the curves, 0, 1, 2, 3, etc., and hence with curve No. 0 provides all of the data needed. Curve No. 0 can be obtained by exposing the positive material in a sensitometer which gives a series of exposures in which the time, t_i, is constant and the intensity, I_i, is varied over the required range and in steps of known magnitude. In case the negative strip has a contrast greater than the total scale of the positive material it will be necessary to make a second print with incident exposure, $N \cdot E_i$ [where $N \cdot E_i = (N \cdot I_i) \cdot t_i$], in order to obtain D_p values for all of the deposits composing the negative strip.

The contact print or prints and the strip exposed in the sensitometer are then developed for equal times, fixed, washed, and dried under exactly similar conditions throughout, after which the resulting densities are read in the usual way.

The method of plotting the data in order to obtain the desired values of D_p is shown in Fig. 8. Curve No. 0 is the same as No. 0 in Fig. 6, being the characteristic curve of the positive material made with I variable and t constant. The densities d'_1,

d'_2, d'_3, etc., read from the contact print, for which the incident exposure on the negative during printing is E_i, are all plotted as ordinates where $\log E = \log E_i = \log I_i \cdot t_i$. The densities read from the second contact print, in case it is found necessary to make a second in order to include all of the densities of the negative strip, are plotted as ordinates where $\log E = \log N \cdot E_i$.

Now

$$D_p = \log E_i - \log E_t,$$

where

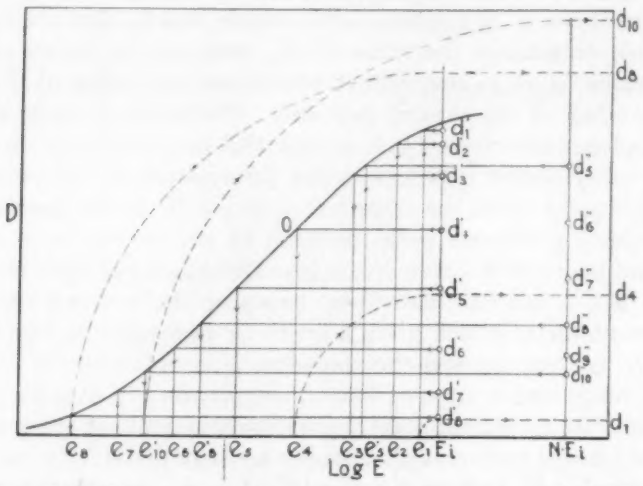
E_i = incident exposure,

and

E_t = transmitted exposure.

The incident exposure (on the negative) in case of the first contact print is E_i, while the transmitted exposure for the various

FIG. 8.



negative deposits, 1, 2, 3, etc., are e_1, e_2, e_3, etc., the values of which are obtained as indicated by the light lines, Fig. 8, the value of e_1 being obtained by reading the log E value of the point of intersection of the curve No. 0 with a horizontal line through d'_1, and similarly for other values.

Therefore

D_p (for deposit No. 1) = $\log E_i - \log e_1 = d_1$,
D_p (for deposit No. 8) = $\log E_i - \log e_8 = d_8$,
D_p (for deposit No. 8) = $\log N.E_i - \log e'_8 = d_8$,
D_p (for deposit No. 10) = $\log N.E_i - \log e'_{10} = d_{10}$, etc.

The values of D_p thus obtained may now be plotted against the log E values for the various negative deposits and the photographic characteristic curve of the negative thus obtained.

The various values of D_p may be obtained graphically by transforming the log E scale upon which the value of e_1, e_2, e_3, etc., are situated into a density scale. This may be accomplished by rotation of the points e_1, e_2, to e_8 about the point E_i as a centre until they lie on the perpendicular through E_i, the points e'_9 to e^1_{10} being rotated about $N \cdot E_i$ as a centre till they lie on the perpendicular through $N \cdot E_i$. Now by projecting the points thus established horizontally onto the density scale the values d_1, d_2, d_3, etc., to d_{10} are obtained. This graphic solution is illustrated in Fig. 8 for the deposits 1, 4, 8, and 10.

This method for obtaining values of D_p involves the assumption that the variation of gradient with quality of radiation transmitted by the deposits being measured is so small as to be negligible. Moreover, the method does not afford means of deciding whether this assumption is or is not valid for any particular case. Therefore this method should be used only when this assumption is known to be in agreement with the facts or after verification by the first method, which shows at once any variation of gradient due to the change in quality of the transmitted radiation.

Now it will be noted that the procedure outlined in the methods just presented is not strictly analogous to that ordinarily followed in obtaining a print from a negative. The quality of a print made under usual conditions must necessarily be influenced by any variation of gamma with wave-length that may exist, for it is obviously impossible to change the time of development for various areas of the print in order to compensate for such variations of gamma. Of even greater importance is the effect of the failure of the reciprocity law upon the quality of a print made in the usual way. In the preceding methods care has been taken to obtain values of D_p which are not dependent upon the absolute values of the I or t factors of exposure, thus eliminating, in so far as is possible, any effect of the failure of the reciprocity law upon such values. Now it is evident that if, for the positive material being considered, a failure of this law exists within the range of intensities transmitted by the various areas of the negative during printing, such failure will have an influence upon the quality of the resulting print. Any method of computing the

tone reproduction obtained by means of such a negative must therefore take account of this failure of the reciprocity law. Since the curves of photographic density obtained by the previous methods are plotted from values from which any effect of reciprocity failure has been specifically eliminated, it follows that if such a curve is to be used in computing tone reproduction the reciprocity failure under the specified conditions of printing must be introduced at some other point in the process. In practice, however, it is found more convenient to obtain for this purpose a photographic characteristic curve for the negative strip in which is included any reciprocity failure that may occur under the conditions that exist in making a print from the negative, such conditions being specified by the absolute value of the I and t factors of the exposure given in printing. With the majority of positive materials when used with negatives of ordinary quality and with the intensity of printing light usually employed in printing, any effect due to the failure of the reciprocity law is negligible, or at least very small. However, it is possible, by using a printing light of very low intensity and a correspondingly long exposure, to observe this effect, a print made in such a way being more contrasty than one made from the same negative by exposing for a shorter time to a source of higher intensity.

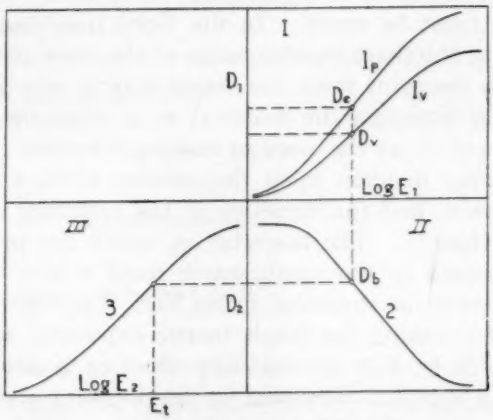
It is evident, from these considerations, that the photographic curve desired, from the standpoint of the reproduction problem, is one that will represent the photographic printing quality of the negative or sensitometer strip under the conditions of actual use. Such a curve must include any effect due to failure of the reciprocity law, and also any effect due to variation in quality of radiation transmitted by the negative, in order to represent the quality of the negative from the practical standpoint. In case these effects do not exist with the materials and under the conditions of printing, the photographic characteristic curve obtained by such a direct printing method will be identical in shape with that obtained by plotting the D_p values of the various deposits as determined in strict conformity with the definition of that term. Such curves, then, represent the actual characteristics of the negative deposits when used under certain specified conditions and enable us to compute the relation between the scale of tone values existing in the original and that reproduced in the positive material by printing from this series of negative deposits under those specified con-

ditions. These curves represent what may be termed the "effective printing characteristics" of the negative strip, and the density values read from such curves, since they may or may not represent actual photographic density, should be referred to as "effective printing densities."

Methods for Effective Printing Density.

In general three groups of data from which three curves may be plotted are required for a solution of this problem. They are as follows: (*a*) The visual density values for the various areas of the sensitometer strip and the corresponding exposure values; (*b*) the density values from a contact print made from

FIG. 9.



the negative strip on the positive material for which the effective printing density values of the negative deposits are desired; (*c*) the density values from a strip of the positive material exposed in the sensitometer and developed along with the contact prints, and the values of the exposures given by the sensitometer to the various areas of this strip. Three methods of reducing these data will be presented, differing slightly in detail. The method most applicable to any particular case will depend upon circumstances and upon the results desired.

The first method will be explained by use of Fig. 9. In the first quadrant are plotted (curve No. I_v) the visual values of density obtained from the negative strip for which the effective printing densities are desired, the ordinates being density and the

abscissæ log E values. A print from this negative strip is made on the desired positive material, and the visual densities of the resulting deposits are measured. In the second quadrant these values are plotted (curve No. 2) against the log E_1 values applying to the corresponding areas of the negative from which the print was made. Let the exposure incident upon the negative strip during printing be designated by E_i. The magnitude of E_i should be such that a just perceptible deposit is obtained on that portion of the positive material printed under the highest density of the negative strip. This is true only if the positive material has sufficient scale for the reproduction of the entire range of contrast existing in the negative. In case the scale is insufficient it will be impossible to obtain a complete printing characteristic from a single print, and two or more prints covering different portions of the negative must be made. In the third quadrant is plotted (curve No. 3) the characteristic curve of the same positive material on which the print from the negative strip was made. This is obtained by exposing the material in a sensitometer to light of the same quality as was used in making the print. The values of the exposure incident upon the various areas are therefore precisely known, and the densities of the resulting deposits are determined visually. The material on which the print is made and that exposed in the sensitometer must receive exactly the same treatment in development, fixing, etc. The highest precision is obtained by making the sensitometric exposures and the contact prints side by side on the same sheet of positive material, thus assuring identical treatment in development and also eliminating any variation in character that may occur from sheet to sheet of the most carefully prepared sensitive materials.

Now the curve in the second quadrant is a true reproduction curve and represents the way in which any scale of tones laid off on the log E_1 axis will be reproduced by use of these negative and positive materials when subjected to exposure and development identical with those used in obtaining this curve. However, since this paper does not deal with the question of tone reproduction, the curve will be regarded from an entirely different standpoint. It may be regarded as the resultant of two curves, the photographic characteristic of the negative and the visual characteristic of the positive material. Since of these two the latter is known, the former may be obtained.

The first problem to be considered is that of finding for any visual density of the negative the corresponding effective printing density. Take any value, D_v, on Curve No. 1, from this print drop a perpendicular to the log E_1 axis cutting curve No. 2 at D_v. The value of D_b, read from the D_2 scale, is the visual density produced on the positive material printed under the visual density D_v of the negative by an exposure E_i incident upon the negative. Now since curves Nos. 2 and 3 were obtained under exactly similar conditions of development, fixing, etc., it is evident that the exposure necessary to produce a density of D_b in one case must be effectively equal to that required to produce the same density in the other case. This exposure, E_t, is obtained by reading the value on the log E_2 scale at the point corresponding to a density of D_b, and is the exposure transmitted by the negative area having a usual density of D_v.

It is evident, then, for the visual density, D_v, that

E_i = incident exposure,

and

E_t = effective transmitted exposure.

Therefore

$\frac{E_t}{E_i}$ = effective printing transmission = T_e,

and

$\log \frac{E_i}{E_t}$ = effective printing density = D_e,

or

$\log E_i - \log E_t$ = effective printing density = D_e.

Now this value D_e is plotted in the first quadrant at the log E_1 value corresponding to D_v, and in similar manner values for other points on curve No. 1_v are obtained which, when connected, give curve No. 1_p, the curve of effective printing density.

Obtaining curves in this way involves considerable computation, although a set of values may be carried through much more rapidly than the explanation of the method would indicate. Since in some cases the position of the curve 1_p is of no particu'ar importance, its shape only being of interest, it is possible to shorten the method somewhat and still obtain all the information necessary. This is true when values of the selectivity coefficient of gradient or of color coefficient are desired, and the values of effective printing density are not important. These latter values are needed only when it is desired to compute the exposure re-

quired to produce a correctly exposed print from a given negative.

Before proceeding further with the discussion, it may be well to demonstrate the method of converting a scale of density values into a corresponding scale of exposure values, for the positive material exposed under the negative deposits. Let E_i be the exposure incident upon the negative during printing and T the transmission of the deposit being considered. The exposure transmitted, E_t, by this deposit and therefore incident upon the positive material in contact with that portion of the negative, will be given by,

$$E_t = E_i \cdot T.$$

Now E_i is constant for all portions of the negative, while T is variable, and hence E_t varies directly as T.

$$\begin{aligned} \log E_t &= \log E_i + \log T \\ &= \log E_i - \log O \\ &= \log E_i - D. \end{aligned}$$

Since E_i is constant, differentiation of the above gives

$$d \log E_t = -dD.$$

Hence any interval on the log E scale is numerically equal to the corresponding interval on the density scale, but of opposite sign. In this way any scale of densities may be converted into a log E scale, or *vice versa*. Of course, if the values of density used are visual, the log E values will also be visual, and similarly for the photographic density values.

Thus

$$d \log E_t \text{ (photographic)} = -dD_p,$$

and

$$d \log E_t \text{ (visual)} = -dD_v.$$

It will be noted that the negative is being regarded simply as a means of impressing a certain series of various exposures on the positive material, and that the visual exposure transmitted by any given area of the negative may be equal to, greater, or less than the photographic exposure transmitted by that area.

Referring now to Fig. 10, the four curves are plotted again as in Fig. 9.

No. 1_v—Characteristic curve of negative (visual).

No. 1_p—Characteristic curve of negative (effective photographic).

No. 2—Reproduction curve (contact print from negative).

No. 3—Characteristic curve of positive material.

The visual gradient of No. 1_v at any value, a, of log E_1, is

$$G_{1,v} = \frac{dD_v}{d \log E_1},$$

the photographic gradient at the same value of log E_1 being

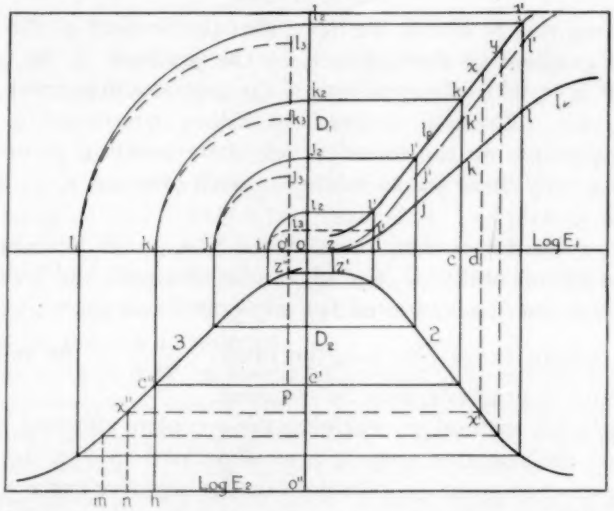
$$G_{1,p} = \frac{dD_p}{d \log E_1},$$

For the same value of log E_1 the gradient of the reproduction curve is,

$$G_2 = \frac{-dD_2}{d \log E_1},$$

and at the point on curve No. 3 where the density is equal to the

FIG. 10.



density of the reproduction curve (No. 2) at the point to which the above expression applies, the gradient is,

$$G_3 = \frac{dD_3}{d \log E_2}.$$

Now, the ratio of the effective exposures (effective E_p) transmitted by any two deposits of the negative strip, the effective printing densities of these deposits being represented by the points x and y on curve 1_p, will be given by the ratio of m to n. The points m and n are located on the E_2 axis, as indicated by the

dotted lines connecting x with n and y with m. Since it has been shown that any d log E value may be converted into a dD value by the expression,

$$d \log E = -dD,$$

it follows that we may write,

$$d \log E_2 = -dD_{1,p}$$

where $D_{1,p}$ = effective printing density.

and E_2 = effective exposure.

Therefore,

$$G_3 = \frac{-dD_2}{dD_{1,p}},$$

and

$$\frac{dD_{1,p}}{d \log E_1} \times \frac{-dD_2}{dD_{1,p}} = \frac{-dD_2}{d \log E_1}$$

or

$$G_{1,p} \times G_3 = G_2.$$

Stating this in words, we have, that the product of the photographic gradient of the negative, by the gradient of the positive material is equal to the gradient of the reproduction curve. This applies only, of course, to gradient values determined at corresponding points on the three curves, corresponding points being defined as any three points related to each other as x, x', and x'', Fig. 10.

It is evident now that, since curves Nos. 2 and 3 can be determined experimentally, G_2 and G_3 can be obtained, and from these values $G_{1,p}$ may be computed for any point, and since $G_{1,v}$ is also known (from curve No. 1_v), the ratio $\frac{G_{1,p}}{G_{1,v}}$, the selectivity coefficient of gradient, may be obtained.

A graphic method of obtaining the complete effective printing curve of the negative strip is also illustrated in Fig. 10. Consider a series of points, i, j, k, and l on the negative curve (visual) No. 1_v. Project these points onto curve No. 2, as indicated by the light full lines, thence onto curve No. 3, and finally onto the log E_2 axis at the points i_1, j_1, k_1, l_1. Now this series of intervals on the log E_2 scale may be transformed into a series of intervals on the D_1 scale according to the relation,

$$d \log E = -d D.$$

This may be accomplished graphically by rotating each point (i, j_1, k_1, and l_1) about the origin O as a centre until they lie on the D_1 scale at the points i_2, j_2, k_2, l_2, and through these points draw

horizontal lines intersecting vertical lines through the points *i*, *j*, *k*, and *l* on curve No. 1. These intersections determine the positions of the points *i'*, *j'*, *k'*, and *l'*, which, when connected, give the curve 1_p the effective printing characteristic for the negative strip. This curve is of the correct shape, and from it and No. 1 values of the selectivity coefficient of gradient and of color coefficient may be obtained. The actual values of effective printing density read from this curve, however, will be correct only when certain conditions in regard to the position of curve No. 3 are fulfilled. Considering any point, *k*, on curve No. 1_v the effective transmitted exposure E_t is given by the value of log E_2 at the point *h*, this point being located as indicated in the diagram. The effective transmission T_p of the deposit represented by the point *k* is, therefore, given by the expression

$$T_p \text{ (for k)} = \frac{E_t}{E_i},$$

$$D_p \text{ (for k)} = \log \frac{E_i}{E_t} = \log E_i - \log E_t;$$

$$\text{also } D_p \text{ (for k)} = \text{the line } c\,k' \text{ (Fig. 10)},$$

$$\text{and } c\,k' = Ok_2 = Ok_1 = c'\,c'' \text{ (Fig. 10)}.$$

$$c'\,c'' = \log E_i - \log E_t.$$

Therefore, if the scale of log E_2 be so constructed with reference to the point *O* or *O''* that when curve No. 3 is plotted the condition that $c'\,c'' = \log E_i - \log E_t$ is satisfied, the derived curve No. 1_p will be correct both in shape and position, and values read from the D_1 scale will be correct values of effective printing density for the deposit considered.

In practice it may be found inconvenient to establish the log E_2 scale as indicated above, and in such cases the same result may be obtained in a slightly different way. Curve No. 3 having been plotted on the log E_2 scale in any arbitrary relation to the point *O''*, establish the point *p* on the line *c'' c'* such that $c''p = \log E_i - \log E_t$. Through *p* draw a line *p o'* perpendicular to and intersecting the *x* axis at *O'*. The points i_1, j_1, k_1, and l_1 must now be rotated about *O'* as a centre until they fall upon the line *pO'* extended, thus establishing the points i_3, j_3, k_3, and l_3. Horizontals through i_3, j_3, k_3, and l_3 intersecting the perpendiculars through *i*, *j*, *k*, and *l* now establish the correct position for the points *i'*, *j'*, *k'*, and and *l'*. Curve No. 1_p (dotted line) is established in this way. No. 1_p (solid) is correct in shape, but is displaced by a shift in the vertical direction from the correct position, this displacement

being due to the fact that $c'c''$ is not equal to log E_4 – log E_t. If there be a point of zero density, z, on the negative curve (No. 1_v) corresponding to which a density Z' exists on the reproduction curve, the intersection of a horizontal through Z' with curve No. 3 will also determine the position of the line O'_p upon which to establish the points i_3, j_3, k_3, and l_3 which determine the D_1 values from which curve No. 1_p (dotted) is plotted. Curve No. 1_p then represents the photographic characteristics of the negative strip as used in printing and includes any failure of the reciprocity law that may occur within its range of contrast when printed in the time t_t, where $E_t = I_t \cdot t_t$.

It will be found unnecessary to actually plot curve 1_p in cases where only color coefficient or selectivity coefficient of gradient is desired This is evident from the following equations. Having plotted curves 1_v, 2, and 3, the gradient values G_{1v}, G_2, and G_3 can be obtained directly and $G_{1,p}$ can be obtained by the relation $G_{1,p} = \frac{G_2}{G_3}$, previously proven.

The selectivity coefficient of gradient $= \frac{G_{1,p}}{G_{1,v}} = \frac{G_2}{G_3 \times G_{1,v}}$.

Therefore the selectivity coefficient of gradient is given by the ratio of the gradient of the reproduction curve (No. 2) to the product of the gradient of the positive material curve (No. 3) by the visual gradient of the negative curve (No. 1). Now in case the gradient is constant these G values become equal to the gamma (γ) values, and hence, for the straight line portion of the curves,

Color coefficient = Selectivity coefficient of gradient

$$= \frac{\gamma_2}{\gamma_{1,v} \cdot \gamma_3} = \frac{\gamma_{1,p}}{\gamma_{1,v}}.$$

Also for this region

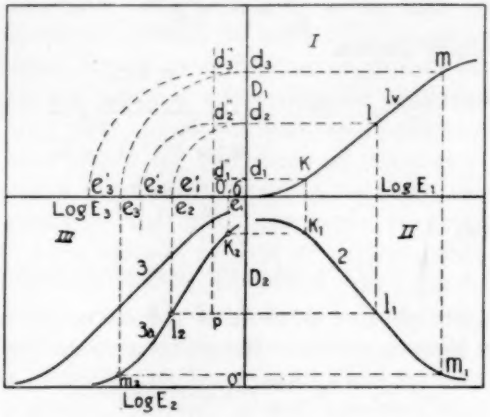
$$\gamma_{1,p} = \gamma_2 \cdot \gamma_3$$

One other method which is very simple and direct for the determination of the color coefficient should be mentioned before closing the discussion. In fact, in practice this method has been found the most convenient for use in many cases. This method gives values of relative gradient only, and applies particularly well to those cases where both the visual and photographic curves of the negative have good straight-line characteristics. Let the intervals of D_1,$_v$ be converted into log E intervals according to the relation,

$$d \log E = -dD.$$

and the values of D_2 obtained from curve No. 2 be plotted as ordinates on this scale. This procedure may be accomplished graphically, the method being illustrated by use of Fig. 11. The curves 1_v, 2, and 3 are plotted as in Figs. 9 and 10. Consider any series of points, k, l, m, etc., on No. 1. Locate the corresponding points k_1, l_1, m_1, etc., on No. 2, as indicated by the dotted lines in the diagram. The densities d_1, d_2, d_3, etc., corresponding to the points k, l, m, etc., are converted into a series of log E values by rotating the points d_1, d_2, d_3, etc., about O as a centre till they lie on the log E_3 scale at e_1, e_2, e_3, etc. This transformation is in accord with the relation, $d \log E_3 = -d\, D_{1,v}$, the difference between any two densities being visual density differences, since these

FIG. 11.



values are derived from curve No. 1_v, which is a visual characteristic curve. Now the intersections of the vertical lines dropped from the points e_1, e_2, e_3, etc., with the horizontal through k_1, l_1, m_1, etc., give the points k_2, l_2, m_2, etc., which, when connected, give curve No. 3a, as shown in the figure. In case curve No. 3 has not been plotted on a log E_2 scale correctly adjusted with respect to O'', the points d_1, d_2, d_3, etc., must first be shifted horizontally till they fall upon the vertical line through O', the position of which is determined as explained in connection with Fig. 10, and then rotated about the point O' instead of O. This is necessary in case it is desired to have curves 3 and 3a lie in correct positions relative to each other, but such is not necessary

if values of color coefficient only are required. Means of placing curve No. 3 correctly with respect to the point O' are discussed in connection with Fig. 10 and need not be repeated here.

Now the gradient at any point on curve No. 3*a* is given by,

$$G_{3a} = \frac{d\,D_2}{d\,\log E_3};$$

but

$$d\,\log E_3 = -d\,D_{1,v};$$

therefore

$$G_{3a} = -\frac{d\,D_2}{d\,D_{1,v}}.$$

Gradient of curve No. 3 is given by

$$G_3 = \frac{d\,D_2}{d\,\log E_2};$$

therefore,

$$\frac{G_{3a}}{G_3} = -\frac{d\,\log E_2}{d\,D_{1,v}},$$

As previously shown

$$\frac{G_{1,p}}{G_{1v}} = \frac{G_2}{G_{1,v}\cdot G_3} = \frac{\dfrac{-\,d\,D_2}{d\,\log E_1}}{\dfrac{d\,D_{1,v}}{d\,\log E_1}\times\dfrac{d\,D_2}{d\,\log E_2}}$$

$$= \frac{-\,d\,\log E_2}{d\,D_{1,v}}$$

Therefore:

$$\phi = \frac{G_{3a}}{G_3} = \frac{G_{1,p}}{G_{1,v}} = \text{Selectivity coefficient of gradient.}$$

and for the straight-line portion of the curve (G = a constant) the G values become equal to the gamma values and we have

$$\chi = \frac{\gamma_{3a}}{\gamma_3} = \frac{\gamma_{1,p}}{\gamma_{1,v}} = \text{Color coefficient.}$$

In practice, unless a graphic solution is desired, curves 1 and 2 are not plotted, but the density values read from the print are plotted against the corresponding visual density values of the negative, which have been laid off on a log E scale according to the expression $d\,\log E = -\,d\,D$. This transformation is most readily accomplished by plotting the visual density values read from the negative on a log E scale laid out from right to left on the x axis and the density values from the print as ordinates. This gives the curve 3*a*, having gradient of the same sign as 3, and the color coefficient is then obtained directly by the relation,

$$\chi = \frac{\gamma_{3a}}{\gamma_3}$$

In the last section of this paper, that dealing with the deter-

mination of the effective printing density, D_e and the various terms expressing the relations between the effective printing characteristics and the visual characteristics of a negative, the same symbols have been used as in the section dealing with the photographic density value D_p determined in accordance with the more rigid definition of that term. This was done in order to avoid a multiplicity of symbols, which so frequently leads to confusion. It should be remembered, therefore, that the values in the last section are understood to be of effective density, transmission, gradient, etc. All values derived from the effective printing characteristic curves, such as curves 1_p in Figs. 9 and 10 therefore depend to a certain extent upon the particular set of conditions used in the determination of those curves. If it is desired to distinguish these terms from the corresponding terms derived from the photographic characteristic curve, such as No. 1_p in Fig. 7, the subscript e should be used. For instance, the value of color coefficient derived as in Figs. 9, 10, and 11 strictly should be called the effective color coefficient and be designated by χ_e (Chi sub e), and likewise Δ_e = selectivity coefficient of effective density, and χ_e = selectivity coefficient of effective contrast, etc. It is not necessary in general, however, to adopt this nomenclature, as the nature of the term may easily be determined by a consideration of the method used in its determination.

Since these values of effective printing densities are dependent upon conditions used in obtaining them, care should be exercised in selecting the proper set of conditions if the results obtained are to be of value in estimating the quality of print that will be obtained from a given negative. It will be noted that in making the contact print from the negative strip the incident exposure E_i was specified to be of such magnitude as to just print through the highest density on the strip. Now in printing a negative the same rule is applied in general; that is, the exposure given is just sufficient to produce a barely perceptible deposit in that portion of the positive material lying under the densest image on the negative. Hence, if the highest density on the sensitometric strip is approximately equal to the highest density on the negative, the values obtained as outlined in the methods presented will apply also to the production of a print from the negative.

The authors realize that a certain degree of artificiality may exist in the definition of some of the terms discussed in this paper.

but with our present knowledge of the subject it seems impossible to entirely eliminate all arbitrary assumptions. It is hoped and expected that as our knowledge of the response of the photographic surface to a given stimulus becomes more complete and precise, it will be possible to eliminate such artificiality and to formulate definitions entirely free from such objectionable factors.

In this paper no effort has been made to present quantitative data, and such statements as are given regarding the characteristics of materials should be regarded as approximate, being introduced only for the sake of illustration. Also in a general paper such as this, it is impossible to deal with all the details of the practical application of the methods discussed. Such a detailed discussion will be given in other sections of this paper, which will appear later, dealing with the application of these methods to specific cases. A very excellent example of the practical application of these methods will be found in the article on "The Sensitometry of Intensification," by Nietz and Huse, which follows this paper. A large amount of data on the spectral sensibility of positive materials and on the color coefficient of negatives produced by the use of various developing agents has already been obtained and will be presented in a later section of the series of which this paper is the first.

SUMMARY.

1. The various functions necessary for the mathematical solution of the problem dealing with the relation between the total visual transmission, T_v, and the total photographic transmission, T_p of any transmitting medium, such as a photographic negative, have been outlined. The functions being (Fig. 2):

J = Spectral energy distribution of the illuminant.
T = Spectral transmission function of the transmitting medium.
V = Visibility function of the retina.
S = Spectral sensibility of the photographic positive surface.
B = Spectral transmission function of the support carrying the transmitting medium.

2. T_v and T_p for a transmitting medium are given by,

$$T_v = \frac{E'}{E} = \frac{\text{Total transmission luminous flux}}{\text{Total incident luminous flux}}$$

$$= \frac{\int_0^\infty J_\lambda V_\lambda T_\lambda \, d\lambda}{\int_0^\infty J_\lambda V_\lambda \, d\lambda},$$

and

$$T_p = \frac{A'}{A} = \frac{\text{Total transmitted actinic flux}}{\text{Total incident actinic flux}}$$

$$= \frac{\int_0^\infty J_\lambda S_\lambda B_\lambda T_\lambda \, d\lambda}{\int_0^\infty J_\lambda S_\lambda B_\lambda \, d\lambda},$$

3. A method for the measurement of T_p analogous to that used for the measurement of T_v has been outlined (Fig. 3).

4. The effect of various forms of the T function upon the ratio $\frac{T_p}{T_v}$ has been discussed (Fig. 4).

5. Verbal terms approximately descriptive of the shape of the T function have been defined as follows: K being a constant:

$T\lambda = K$ (From 400$\mu\mu$ to 700$\mu\mu$)—Visually non-selective or neutral.
$T\lambda \neq K$ (From 400$\mu\mu$ to 700$\mu\mu$)—Visually selective or colored.
$T\lambda = K$ (From 280$\mu\mu$ to 500$\mu\mu$)—Photographically non-selective.
$T\lambda \neq K$ (From 280$\mu\mu$ to 500$\mu\mu$)—Photographically selective.

6. Terms relating the visual and photographic characteristics of a single deposit and of a series of deposits such as compose a photographic negative have been formulated and named as follows (Fig. 5):

(A) For a single deposit or transmitting medium,

$\frac{D_p}{D_v}$ = Selectivity coefficient of density = Δ (Delta).

(B) For a series of deposits, such as a negative,

$$G_v = \frac{d\,D_v}{d\,\log E} \text{ and } G_p = \frac{d\,D_p}{d\,\log E}$$

are the visual and photographic gradients at a given value of exposure, E.

(a) If $\frac{G_p}{G_v}$ varies with E, then

$\frac{G_p}{G_v}$ = Selectivity coefficient of gradient = ϕ (Phi).

(b) If $\frac{G_p}{G_v}$ = is constant for all values of E (or over the range of E considered) and G_p and G_v vary with E, then,

$\frac{G_p}{G_v}$ = Selectivity coefficient of contrast = K (Kappa).

(c) If $\frac{G_p}{G_v}$, G_v, and G_p are all constant for all values of E (or over the range E considered), then,

$\frac{G_p}{G_v} = \frac{\gamma_p}{\gamma_v}$ = Color coefficient = χ (Chi).

7. Methods for the determination of D_p either of a single deposit or for a series of deposits are outlined.

(*A*) A general method eliminating errors due to failure of reciprocity law and variation of gamma with wave-length (Figs. 6 and 7).

(*B*) A less general and shorter method based on assumptions that must first be proved by use of (*A*) (Fig. 8).

8. Effective printing density, D_e, is defined as a special value of the photographic density which may be slightly different from D_p as previously defined, in that values of D_e are determined by methods analogous to those used in making a contact print from a negative, and therefore are influenced by any failure of the reciprocity law and by variations of gamma with wave-length. Such values in general apply only under a certain set of conditions.

9. Methods for the determination of D_e for a series of deposits are outlined.

(*A*) An algebraic solution giving values of D_e and thus the complete effective printing characteristics of a negative (Fig. 9).

(*B*) A graphic solution giving the complete effective printing characteristic and consequently the D_e values for the series of deposits composing the negative (Fig. 10).

10. Both of the above methods involved the use of four curves.

1_p—Effective printing characteristic of the negative.
1_v—Visual characteristic of the negative.
2 —Reproduction curve (plotted from densities of contact print).
3 —Characteristic curve of positive material.

It is shown that (G being used as the general symbol for gradient)

$$G_{1,p} \times G_3 = G_2,$$

and that

$$\kappa = \text{Selectivity coefficient of effective contrast} = \frac{G_{1,p}}{G_{1,v}} = \frac{G_2}{G_3 \times G_{1,v}}.$$

Or, if these terms are constant, that

$$\gamma_{1,p} \times \gamma_2 = \gamma_3.$$

$$\chi = \frac{\gamma_{1,p}}{\gamma_{1,v}} = \frac{\gamma_3}{\gamma_2 \cdot \gamma_{1,v}} = \text{Effective color coefficient.}$$

11. A direct method for the determination of effective color coefficient, χ, is outlined (Fig. 11).

$$\chi = \frac{\gamma_{3a}}{\gamma_2} = \text{Effective color coefficient,}$$

where γ_{3a}, is the gamma of curve *3a*, which is plotted directly from data obtained from curves 1 and 2, previously mentioned.

ROCHESTER, N. Y.,
October 8, 1917.

Institute for the History of Science. B. RUSSELL. (Circular letter, Patent Office Society, Washington, D. C., November 12, 1917.)—It is an admitted fact that the art of recording progress of scientific achievement in a form readily available for the use of the investigator has been developed in this country to a much less degree than in Europe. At the present time the inferiority in this important adjunct to progress in the advancement of science is fully appreciated, and within the last few months the expediency of founding an institution devoted on broad lines to this end has received considerable attention.

As outlined by Dr. George Sarton in *Science* for March 23, 1917, the history of science deals with so large a part of the intellectual development of the race that it should attract the interest of every thinking person. Such an interest is already manifest among an ever-increasing number of scientists and technicians. The field is too broad to be adequately covered by separate departments in any of our universities. This can be accomplished only by an institution devoted strictly to this purpose and adequately equipped for the great work that needs to be done. Such an institution should open its doors freely to the few who are sufficiently advanced to profit by its help, but it should not be hampered by any question of degrees or credits, remaining free to do for the advanced student what it feels will be of service in establishing the highest standards of research and scholarship.

Collateral to its efforts to increase the efficiency of the patent service, the Patent Office Society recently passed a resolution relating to a proposed Institute for the History of Science, for which a location at Washington is advocated, of the general character proposed by Doctor Sarton and others. Among the activities of such an institute recommended by Doctor Sarton are the following: (1) To

offer to qualified students the best equipment for work, and the advice, assistance, and encouragement of a small corps of experts in the history of science. (2) To afford to universities, libraries, and scholars the opportunity to acquire at cost photographs of important manuscripts, documents, and objects for leisure study. (3) To offer to scientists interested in history, to historians interested in science, and to cultivated philosophers a meeting place worthy of their respect; a clearing-house where all matters of common interest to them would be centralized, examined, and eventually made known to the world. (4) To establish collections of prints, instruments, and all other early material bearing on the history of pure and applied science. This activity would in course of time expand into a department of enormous importance, as is clear to any one who has visited the Conservatoire des Arts et Metiers in Paris, the Science Museum in Kensington, or the Deutsches Museum in Munich, foundations with which we have nothing to compare in this country. (5) To publish two journals; one of a popular nature, the other of the highest scientific character.

Such an institute would not rival any department in our universities. It can and should set a higher standard of scholarship by reason of its independence, and it should be looked upon as a valuable aid by every university in the country and abroad, and as a source of supply of material which no university or library can furnish.

The Prevention of Brittleness in Electroplated Steel Springs. T. S. FULLER. (*Proceedings of the American Electrochemical Society*, October 3–6, 1917.)—One of the serious problems that confronts the makers and users of non-corroding steel springs is the brittleness produced therein during electroplating. The embrittlement is generally conceded to be caused by the nascent or atomic hydrogen which is liberated at the cathode. The fact that iron takes up nascent hydrogen at low temperatures and is made very brittle thereby was developed by a number of investigators about 1870 to 1880. Numerous researches showed that the flexibility and elasticity of iron wire and steel springs are greatly decreased by pickling, and that the effect is the more marked the thinner the material. Electrolytic iron may contain nearly 250 times its volume of hydrogen, while the commercial iron averages only one-half of its volume. Tests were made of the breaking strength of seven untreated springs; then tests were made of similar springs electrically copper plated, pickled in sulphuric acid, and tinned by dipping in molten tin and then copper plated. The pickling and the copper plating both cause brittleness, but tin dipping before copper plating is found to prevent embrittlement entirely. Steel springs may be dipped in molten tin at a temperature of 260° to 300° C. without appreciably changing their mechanical properties.

THE APPLICATION OF MECHANICAL DIFFERENTIATION TO ENGINEERING PROBLEMS.

BY

ARMIN ELMENDORF, M.Sc.,

Engineer in Forest Products, U. S. Forest Products Laboratory, Madison, Wis.; Member of the Institute.

In its application to engineering problems, mechanical differentiation is almost always concerned with determining acceleration so that the latter may be substituted in some equation connecting it with force and mass. The significance of the law that force is equal to the product of mass into acceleration cannot be overemphasized. Every object in motion, be it a ball, projectile, automobile, or locomotive—in fact, whatever has mass, and hence every conceivable body—pursues its path in absolute accord with the dictates of this law. A street car is either increasing its speed, running at a constant speed, or is being decelerated. Each of these motions is the result of the simultaneous action of several external forces. The resultant force at the tread of every wheel may be resolved into a vertical and horizontal component. The total vertical or upward force is equal to the total downward force or the weight of the car; hence, there is no motion in this direction. On the other hand, the resultant of all the horizontal forces acting on the car may be acting forward, so that it acquires motion, and this motion is continually increased until the horizontal forces balance, when the car proceeds at a constant or uniform speed. Finally, if the sum of the forward or impelling forces is less than the sum of the retarding forces, the speed falls off until motion ceases. In every instance the resultant force acting on the car, producing a change in its speed, is equal to the product of the mass of the car into its acceleration.

TRAIN RESISTANCE.

The illustration of the street car is particularly pertinent in that it suggests an engineering problem whose solution will be enhanced by mechanical differentiation; namely, the problem of train resistances. Many tests have been made to determine train resistance, but these have always depended upon direct-force readings from a dynamometer connecting the locomotive with the train. Inaccuracies seem to be inseparable from such tests. It

is troublesome to obtain the grade of the track for any considerable distance, which, if it is not taken into consideration, must necessarily introduce error, because a grade either demands an increase in the draw-bar pull, or, in the case of descent, it diminishes the pull. Secondly, the readings being taken by observers on the train, the changes in speed cannot be known, so that the force required to accelerate the train is read in with the draw-bar pull as train resistance.

A resort to the purely kinematical relations of distance, velocity, acceleration, and time has been suggested, eliminating entirely all direct measurements of force. By allowing the car to coast upon a section of level track, the distance-time, or even the speed-time, curve may be obtained with suitable instruments. A double differentiation of the former curve with a differentiating machine or a single differentiation of the latter yields the acceleration-time curve, and all that remains to be done to find the total car resistance at any instant is to multiply the mass of the car by the acceleration at that instant. Then, by referring back to the speed-time curve, the speed at the same instant may be learned, and from these data a speed-resistance curve could be drawn. Such information is especially valuable for curves in the track. The civil engineer must know curve resistance in laying out a road, to be able to establish permissible grade.

The beauty of an investigation on the order of that outlined is that another item of great importance may be studied; namely, power consumption. What is the actual horsepower consumed in train resistance? Technical terminology defines power as work per unit of time. The foot-pound per second, as well as the horsepower, is a unit of power. Knowing the total retarding force at any instant and the velocity at the same instant, it is only necessary to multiply the two to obtain power consumption at that instant due to train resistance. If the unit of force is the pound and of velocity a foot per second, then the product of force into velocity gives power in foot-pounds per second, which, divided by 550, gives horsepower. Hence a power-consumption speed curve could be obtained.

ELECTRIC CAR EFFICIENCY.

Another problem bearing on rolling stock is the determination of the horsepower of an electric car under starting conditions, and its efficiency as a machine under the same conditions. Taking

the ordinary definition of efficiency as the ratio of useful power or power output to power input, we see that for the electric car as a machine, useful power is the power not expended in overcoming friction, hence available to pull trailing cars or for acceleration, while the latter is the total electrical power delivered to the motors. Efficiency is thus also a measure of the ability of the car to pick up speed under a certain power consumption. Clearly, vehicle efficiency defined in this way would be zero when the car is running at a constant speed. Contrary to the usual efficiency relations, the efficiency of a vehicle of this kind would probably be a maximum soon after starting instead of near its highest speed as with most machines used for motive purposes.

To determine vehicle efficiency it is necessary again to resort to the kinematical relations existing between speed, acceleration, and time. By mounting a sensitive speedometer on the car and reading it at definite small time intervals while the car is "getting up speed" the data for a speed-time curve could be obtained. A record of power consumption must also be taken from the wattmeter. Then, differentiating to get the acceleration curve, and proceeding from it through the force-velocity relations, we arrive at "useful power." The ratio of this power to that given by the meter would be vehicle efficiency. From it any efficiency-speed curve could be drawn for any setting of the starting control. The total power delivered to the motors, it will be seen, is thus consumed in overcoming friction (internal, track, and air resistance), in accelerating the car, and in heat loss in the armature.

Correction for rotating parts would have to be made, but this presents no great difficulty. The only step that must be taken is the determination of the moments of inertia of the rotating parts, which could be done experimentally or approximately computed. Besides being given a translatory acceleration, these machine parts are given a rotational acceleration, which also consumes power. The relation between torque, T, angular acceleration, α, and moment of inertia, I, about the axis of rotation is given by the equation, $T = I\alpha$. The angular acceleration and moment of inertia being known, the corresponding torque may be computed. If n is the speed of rotation in revolutions per second, the power, P, is expressed by the equation $P = 2\pi Tn$, which is the instantaneous power required to produce the angular acceleration, α, corresponding to any particular speed of rotation, n.

AUTOMOBILE EFFICIENCY.

In an automobile considered as a machine, the power input would be the brake horsepower of the engine, and the useful power would be the same as that of the electric car; namely, the power available for acceleration. The former is not known, since we are not certain that the running conditions, when mounted in the automobile, are the same as those when the engine is on the test-block. Neglecting the slight difference in power lost in the gears due to difference in power transmitted when running idle and under full load, we may determine many interesting features of automobile performances. A coasting run on a level and smooth road will give all the data for the determination of the total friction power at various speeds, the problem being identical to that outlined for train resistance. Now, starting the automobile over the same road and under the most effective starting conditions in regard to throttle and spark control will furnish the data for the useful or acceleration power curve. The sum of the two is engine power at the clutch, and the ratio of the useful power to the total power is the automobile efficiency. Efficiency curves could be drawn for various combinations of throttle and spark.

ROAD RESISTANCE TO TRAFFIC.

By allowing an automobile to coast over various road surfaces and drawing up the resistance curves as before, valuable information could be obtained upon the power consumed in travelling over the different surfaces. Possibly road taxes could be justified in this way.

AIR RESISTANCE TO FLIGHT.

The resistances to flight of aeroplanes of different designs merit considerable study. Experiments upon models placed in "wind-tunnels" through which a blast of air is sent by artificial means can give only approximate results on account of the miniature size of the models and the confinement of the air currents set up by the obstruction. The need for information on full-size machines in flight is evident.

By means of two transits, one for observing horizontal displacements of a gliding aeroplane, and the other for noting changes in altitude, all the data for the distance-time curve may

be obtained. Proceeding from it through double differentiation to the acceleration-time curve, and then to the power curve due to changes in altitude, some of the most valuable data concerning airplane performance become available; namely, the power necessary to overcome head resistance under various speeds.

STRESSES IN BEAMS, GIRDERS, AND SLABS.

The branch of mechanics covered by the strength of materials furnishes several important technical problems whose solution may be enhanced by mechanical differentiation. Due to the indeterminate nature of wall loading, for example, theoretical stress computation can yield only approximate results. If, however, instead of starting with the loading, we arrive at the external or bending moment at any section of a girder through differentiation of the deflection curve, greater certitude attaches to the stresses determined. The actual stresses computed in this way may be compared with the theoretical stresses.

Since the second derivative measures the rate of a rate, it measures curvature, and, in the case of beams, curvature indicates bending and stresses. The lowering of the neutral axis of a girder relative to its position in the unloaded condition is readily determined, so that the deflection curve is known and may be plotted to an enlarged scale of ordinates. Subsequent to the double differentiation involved, no particular difficulty should be encountered. Remembering the relation between external or bending moment and stresses expressed by the flexure formula, and the relation between the former and curvature, we have

$$M = \frac{SI}{c} = EI\frac{dy^2}{dx^2} \quad \text{or}$$

$$S = Ec\frac{dy^2}{dx^2} \qquad \text{where}$$

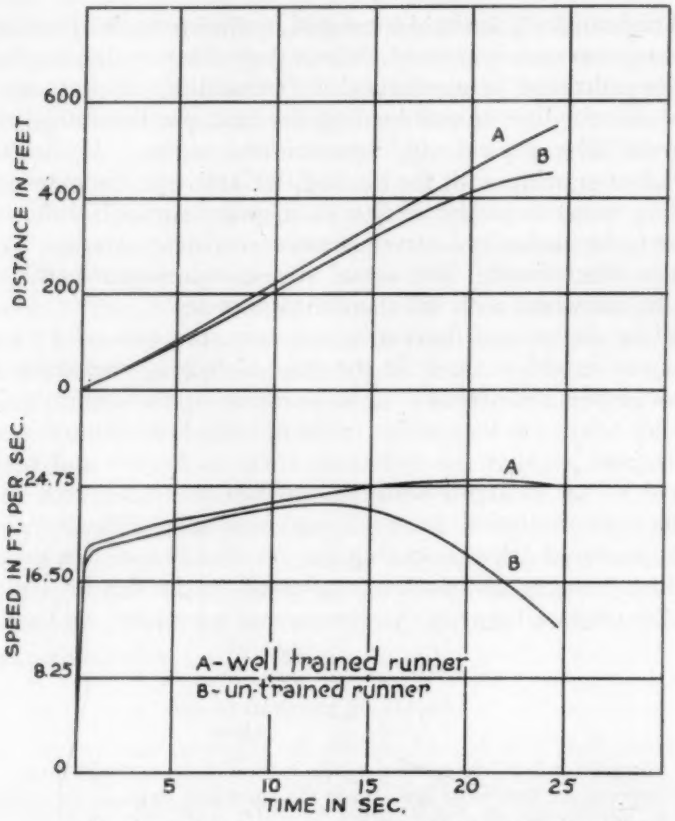
M = External or bending moment at the section under consideration.
S = Stress in the outermost fibre, hence the maximum stress in the section.
I = Moment of inertia of the section.
c = Distance from the neutral axis to the outermost fibre.
E = Modulus of elasticity of the material.
y = Deflection.
x = Distance along the neutral axis.

It will be seen that this solution may also be applied to the vexing problem of flat slabs, since the troublesome and unknown moments of inertia fall out entirely.

MUSCULAR POWER OF THE HUMAN BODY.

From tests conducted upon students performing various exercises, the author was able to compare graphically the power and endurance of men whose physical training varied over wide limits.[1] Distance-time curves were obtained for running uphill,

FIG. 1.



Development of endurance or power curves for men running uphill.

weight-lifting, and swimming. A single differentiation yielded the speed curves. In the case of the men running uphill vertical speed multiplied into the weight of the runner gave this external power. The maximum attained by any one runner over a distance of 500 feet up a 10 per cent. grade was a little more than

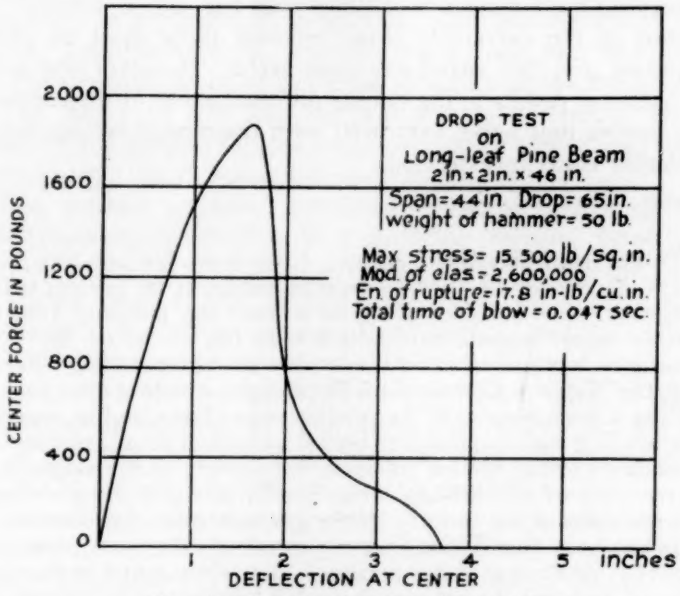
[1] *Scientific American Supplement* for August 11, 1917.

three-quarters horsepower. Typical endurance curves developed in this way are shown in Fig. 1.

STRESSES IN IMPACT.

In a series of impact tests conducted at the United States Forest Products Laboratory at Madison, Wis., in 1915, upon timber beams, by dropping a 50-pound weight upon the centre of the beam in a Hatt Turner impact testing machine, the author

FIG. 2.



Force-deflection curve for a timber beam in impact.

obtained deflection-time curves for a number of beams broken by a single blow. The second derivative of these curves yielded acceleration which, substituted in the formula

$$F = W_t - (W_t + \frac{17}{35} W_b) \frac{1}{g} \frac{ds^2}{dt^2}$$

gave the forces to plot force-time curves. In the equation, F is the centre force, W_t the weight of the tup, here 50 pounds, W_b is the weight of the beam, and s is vertical displacement. By scaling the forces corresponding to each deflection, the force-

deflection curves for impact loading were drawn, and by substitution in the flexure formula the maximum stresses set up in the beam by the blow were obtained.[2] A typical impact force-deflection curve is shown in Fig. 2.

VALVE MOTION.

Innumerable cases arise in machine design in which it is desired to know the magnitude of forces that will produce certain motions. One of these is given by the valve stem in a high-speed engine. The size of the spring necessary to avoid hammering by keeping the follower in contact with the cam is wanted. On account of the extremely small motions these must be greatly magnified, and this introduces some error. However, the author has obtained results in the double differentiation of displacement-time curves that agree very well with theoretical results for the particular cams investigated.

MADISON, WISCONSIN, September, 1917.

Toluol from City Gas. ANON. (*The Iron Age*, vol. 100, No. 21, p. 1275, November 22, 1917.)—In anticipation of the present national emergency, there has been going on without any publicity a development in toluol manufacture which bids fair to be of the utmost importance to the nation in the supply of trinitrotoluol. Early in 1915, the Koppers Company of Pittsburgh, which at that time was building a large number of by-product coke plants, and in connection with which it was also building benzol and toluol plants, started in the laboratories of the Mellon Institute, Pittsburgh, an investigation into the recovery of toluol from carburetted water gas, the gas made in all large cities of the country by the gas companies for domestic use.

It has been found that every by-product coke oven plant in the country is producing or has arranged to produce toluol to the utmost capacity, and that the remaining needed toluol must be secured from city gas. The Pittsburgh By-Product Coke Company, an operating company associated with the Koppers Company, has carried out a plan in conjunction with the gas-light company at Washington to erect the first plant at the West station of that company to effect the removal of toluol from 5,000,000 cubic feet of carburetted water gas per day. This plant was placed in operation on July 14, 1916, and has yielded since that date 200,000 gallons of toluol. While this plant was the first to use this process, and many improvements increasing the efficiency and economy of operation have been introduced, it proved a commercial and technical success, equalling the results promised by laboratory methods. Many of these "stripping" plants are in operation in various cities, and others are in preparation.

[2] JOURNAL OF THE FRANKLIN INSTITUTE, December, 1916.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

PHOTOGRAPHIC RESOLVING POWER.[1]

By Kenneth Huse.

[ABSTRACT.]

PHOTOGRAPHIC resolving power is defined in terms of the distance by which two minute images lying adjacent to one another must be separated in order that, when photographed, they may be distinguishable as separate images and may not merge into one in consequence of the grain structure of the emulsion.

The object of this investigation was to determine the influence of the specific factors, exposure, development, and wavelength of light on photographic resolving power.

The method employed consisted of photographing a fan-shaped converging grating in a reducing camera, fitted with a highly corrected telescopic objective. The measurements of the minute images thus formed were made on a micrometer microscope. Since the spacing of the grating and the scale of reduction are known, a numerical expression for resolving power is found. The sensitive material used was Seed Lantern plates.

The errors involved in the method, due to the use of a lens and to the fact that the measurements introduce the personal equation to a certain extent, are proved negligible.

The results of experiments on the effect of exposure show that resolution is extremely sensitive to this factor, there being a critical value where best resolution is manifested, serious over- or under-exposure being detrimental. It was also found that there is an optimum time of development for best resolution, so that it seems that an exposure such that the densities lie on the straight-line portion of the characteristic plate curve, and development to a gamma of unity, yield highest resolving power.

Investigation showed that the reducer or the developer employed had great bearing on resolution. Twenty developers were

* Communicated by the Director.

[1] Communication No. 61 from the Research Laboratory of the Eastman Kodak Company, published in *Journal of the Optical Society of America*, July, 1917, p. 119.

investigated. The results obtained showed variation in resolution values varying from 47 to 77, due to the developer.

With regard to the effect of the wave-length of the incident light, resolution was best for light of short wave-lengths, the resolution decreasing to a minimum in the green and increasing again in the red, though not to as high a value as with blue light. In these experiments three types of photographic emulsions—ordinary, orthochromatic, and panchromatic—were used.

The Belgian Coal and Coke Industry. ANON. (*Coal Age*, vol. 12, No. 17, p. 713, October 27, 1917.)—During the years that immediately preceded the war, Belgium produced, in round figures, 24,000,000 metric tons of coal a year. About 1,350,000 tons of this was coked, yielding a trifle more than 1,000,000 tons of commercial coke, including breeze sold for domestic use. All coke was, of course, by-product coke, as none other has been made in Belgium since 1892 or 1893.

Belgium was a pioneer in the by-product industry. The oldest by-product company now in existence is the Société Anonymé du Charbonnage des Produits, at Flénu, Belgium, which was incorporated in 1856 for the mining of coal and the manufacture of by-products. That company may have become better known abroad as a coal company than as a by-product concern, but this was due to the extraordinarily fine natural condition of its coal deposits, which enabled the company to pay big dividends earned in mining and selling coal while meeting the stress of developing the by-product department of its business. Regardless, however, of the trying period of development, the Produits Company never ceased for a single day, since 1856, to make by-products; and the first aniline colors ever put on the market were made at Flénu by this company at a time when its coke and by-product department was managed by the noted Belgian chemist Neyrincks.

With the advent of the Coppée vertical-flue coke oven, the Produits Company became a decided factor in the by-product industry. That was about 1870, at a time when Germany had only beehive coke ovens and when all coke made in Belgium was produced in retort ovens of the original Coppée design. Not only was Germany later than Belgium in eliminating its beehive ovens, but even to this day there is not in Germany a single coke oven which is not of the vertical-flue kind first invented by Coppée, a Belgian, or the horizontal-flue type developed by Solvay and Semet, the former a Belgian, the latter a Frenchman, both living to-day. Many persons in this country believe, even among those of the by-product industry, that the by-product oven is of German origin and development. To this day the Belgium coke ovens have always kept at least one step ahead of all others.

NOTES FROM THE PHYSICAL LABORATORY OF THE UNITED GAS IMPROVEMENT COMPANY.*

A NEW NEUTRAL TINT AND A VARIABLE TINT SCREEN.

By E. Karrer.

A NEUTRAL tint screen has been constructed using small glass bars, between which is laid a very thin layer of some black opaque material. The screen has a very high maximum transmission, determined only by the transmission of the optical glass used to make the bars and the thickness of the interposed opaque material. The screen may also be made into a variable tint screen by replacing the opaque material by some colored transparent medium. As the angle between the screen and the incident beam of light is altered, more of the light is cut out by the opaque screen in the first case, and a greater portion of the light is transmitted through the colored medium in the second case.

A CONVENIENT LABORATORY CONDENSER FOR EXPERIMENTAL PURPOSES.[1]

By E. Karrer and H. S. Newcomer.

A CONDENSER for use in spectroscopy with the spark is described, in which pyrex glass beekers are used as the dielectric, immersed in a salt solution for the conductor. The performance of the condenser has been found for this purpose to be very satisfactory.

ON THE LUMINESCENCE OF RADIOACTIVE MATERIALS.[2]

By E. Karrer and D. H. Kabakjian.

A STUDY of the luminescence of phosphorescent zinc sulphide when excited by radioactive substances has been made and a more detailed study of the general phenomena of luminescence of materials due to radioactivity has been carried out. The decay

* Communicated by the Manager.

[1] In collaboration with the Phipps Institute, University of Pennsylvania.

[2] In collaboration with the Physical Laboratory, University of Pennsylvania.

curves (brightness *vs.* time) have been plotted for many samples of luminous substances. A series of curves of this character has also been made where the percentage of the radioactive material has been changed. The temperature effects upon the luminescence have been studied. The results seem to be in more general accord with Rutherford's theory than shown by previous workers. Certain new applications of the luminescence of these radioactive materials will be given in the near future.

THE APPLICATION OF GRAPHICS TO GAS MIXTURES.

By Edward J. Brady.

TRILINEAR coördinates to express the characteristics of alloys consisting of three different metals were first used by Professor Thurston in 1877.

For a better illustration of their value, we may cite their use in the theory of color where any integral color may be represented by a point on a triangle, each corner representing 100 per cent. of one of the three primary sensations.

The fact that this method of graphical representation can be admirably applied to the determination of the characteristics of gas mixtures seems to have been overlooked.

In a mixture of three gases the heating value of the mixture is equal to the sum of the products of the percentage of each constituent multiplied by its respective heating value. This is also true of specific gravity, as well as the amount of air necessary for complete combustion.

It follows from the above that if on each of the three corners of a "gas mixture triangle" we erect perpendicular lines proportional to the heating value of the constituent at that corner, the upper ends of these lines will determine a plane. This plane, which we may call the heating value plane, will, in general, make an angle with the plane of the paper. Contours, or lines of equal heating value, drawn upon this plane will be straight parallel lines, making angles with the sides of the triangle, depending upon the heating value of the particular gases mixed. Such lines are the loci of an infinite number of mixtures of the three gases represented, all having the same heating value.

Similar systems may be drawn for specific gravity and air required for complete combustion.

The latter system will, in general, be almost parallel with the heating value contours, because of the fact that heating value is roughly proportional to the number of O_2 atoms required for complete combustion.

Specific gravity contours or lines of equal gravity generally cross the heating value lines at certain angles. It is thus possible to eliminate one of these variables from experiments on gas mixtures.

Travelling along one of the gravity contours changes the heating value but not the gravity, and *vice versa.*

These lines are all straight because of the linear relation between the particular characteristics so chosen, viz., heating value, gravity, etc., and the quantity of gas involved.

However, other characteristics of the mixture may also be represented, as velocity of inflammation by curved lines.

The "gas mixture triangle" is not limited to pure gases. We may determine the characteristics of such gases as coal gas, water gas, and oil gas in the ordinary way, using these values to construct a triangle, and proceed as above. The quality of a mixture may be decided upon and its position on the diagram located at a point. A circle drawn with the point as a centre will establish a tolerance outside of which the mixture must not fall. Other uses will suggest themselves.

The Effect of Mouthpieces on the Flow of Water Through a Submerged Short Pipe. F. B. Seely. (*University of Illinois Bulletin,* No. 96, April 30, 1917.)—A knowledge of the extent of the loss due to contraction or expansion of a stream is of considerable importance in a variety of hydraulic problems. Comparatively little experimental work has been done to determine the value of conical mouthpieces of various angles and lengths in reducing the entrance and discharge losses of a submerged pipe, particularly for mouthpieces of the sizes and proportions comparable with those met in engineering practice. For example, it may be possible, by due attention to the shape and angle of connections and intakes, to increase the flow through the suction and discharge pipes of low-head pumps, through large valves, and a number of other hydraulic devices.

Losses from this cause are difficult to estimate and easy to overlook. Even where such losses are in themselves of little consequence as compared with other quantities involved, they may have a considerable influence upon subsequent losses on account of the turbulent motion started by the contraction or expansion. The flow of water usual in engineering practice is more or less turbulent. The general

equation of energy, or Bernoulli's theorem, so generally used in hydraulics, applies only where the particles of water move with uniform velocity in parallel stream-lines. Although this condition of flow seldom occurs, satisfactory analyses may often be made by using an average velocity and introducing empirical constants. However, a very slight change in the conditions under which flow takes place may cause, in some cases, a large difference in the action or behavior of the water. There is, therefore, always danger in extending the use of experimental data or empirical constants to apply to conditions of flow quite different from those under which the data were obtained.

To determine the losses of head under varying conditions of flow, a tank with a partition forming two compartments was used. A cast-iron short pipe, 22½ inches long, of 6 inches bore, was attached by a flange near the middle to the partition separating the two compartments of the tank, allowing the pipe to project into each compartment. This tube was threaded at each end so that a mouthpiece could be screwed on either end or both ends. The cast-iron conical mouthpieces which were screwed at the ends of the 6-inch pipe were, at the small ends, of the same cross-sectional area as the pipe with varying angles of flare.

As applying to conditions likely to be met in engineering practice, taking h = total head, h^1 = loss of head at entrance, v = mean velocity in the pipe, and, c = coefficient of discharge:

(*a*) In an inward projecting tube (no mouthpiece): $h^1 = 0.62\ v^2/2g$ instead of $0.93\ v^2/2g$ as usually assumed, giving $c = 0.785$ instead of 0.72 as given in $h^1 = (1/c^2 - 1)\ v^2/2g$. Flush tube (square entrance): $h^1 = 0.56\ v_2/2g$ instead of the customary $0.49\ v^2 2g$, with $c = 0.80$ instead of 0.82, as given by nearly all authorities.

(*b*) In an inward projecting tube with conical mouthpiece: h^1 may be as low as $0.165\ v^2/2g$ if the flare is between 30 and 60 degrees (angle with axis), with an area ratio of mouthpiece to pipe between 2 and 4, and the value of $c = 0.915$.

(*c*) For mouthpieces with a flare of 20 to 90 degrees and area ratio to 4: $h^1 = 0.20\ v^2/2g$, and there is little advantage in making an entrance mouthpiece longer than corresponds to an area ratio of 2 and a flare angle greater than 10 degrees.

(*d*) The amount of velocity head recovered at the discharge end decreases rather rapidly as the angle of divergence increases from a total angle of 10 to 40 degrees. At or near 40 degrees the velocity head recovered falls approximately to zero.

(*e*) A conical discharge mouthpiece with a total flare angle of 10 degrees and area ratio of 2 will recover 0.435 of the velocity head in the pipe, which is 58 per cent. of the theoretical amount possible of recovery.

(*f*) An entrance mouthpiece tends to promote smooth flow in the pipe, and greater velocity head recovery is possible when the pipe is provided with mouthpieces at both ends.

THE FRANKLIN INSTITUTE.

(Proceedings of the Annual Meeting held Wednesday, January 16, 1918.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, January 16, 1918.

PRESIDENT DR. WALTON CLARK *in the Chair.*

Mr. Charles E. Bonine, Acting Chairman, Committee on Science and the Arts, reported the condition of the work of the Committee.

The tellers of the election, Messrs. Jennings, Colvin, and Picolet, submitted the report of the ballots cast for President, Vice-president, Treasurer, and members of the Board of Managers, and the following gentlemen were declared duly elected to the respective offices:

Walton Clark, President (to serve one year).

Louis E. Levy, Vice-president (to serve three years).

Cyrus Borgner, Treasurer (to serve one year).

Charles Day, Kern Dodge, Alfred W. Gibbs, George R. Henderson, George A. Hoadley, Isaac Norris, Jr., Lawrence T. Paul, James S. Rogers, Managers (to serve three years); Gellert Alleman, Manager (to serve two years).

The President presented a statement of the work of the Institute for the fiscal year ending September 30, 1917, with the reports of the various committees of the Institute and Board of Managers.

Doctor Hoadley, on behalf of the Committee on Science and the Arts, introduced Mr. Max Levy, of Philadelphia, to whom had been awarded the Edward Longstreth Medal of Merit for his Hæmocytometer.

The President presented the Medal and accompanying document to Mr. Levy, who thanked the Institute for the honor conferred upon him.

The paper of the evening was presented by W. P. Mason, M.D., LL.D., Professor of Chemistry, Rensselaer Polytechnic Institute, Troy, N. Y. The lecturer pointed out the dangers that arise from faulty camp construction and regulation, whether the occupants be soldiers or laborers. These dangers may not be confined to those in the camp, but may extend to distant communities in the same general district. Consideration was given to methods for caring for fecal material; horse manure; kitchen refuse and general garbage; fly-transmission of disease; incineration and types of incinerators; policing of camps; protection of watersheds; protection of camp sites; camp water supplies; portable laboratories for water analysis; European army standards for water; sterilization and related sanitary problems. The subject was illustrated by lantern slides.

After a discussion, the thanks of the meeting were extended to the speaker. On motion, duly seconded, the thanks of the Institute were also extended to the tellers of the election for their services.

Adjourned.

GEORGE A. HOADLEY,
Acting Secretary.

REPORT OF THE PRESIDENT

FOR THE FISCAL YEAR ENDING SEPTEMBER 30, 1917.

To the Members of The Franklin Institute:

I am instructed by your Board of Managers to report to you upon the Institute's work during the Institute year last past. This writing is the report.

It is impossible to write any story of accomplishment during the year just past without frequent reference to the great event of that year—the entry of the United States into the world war. And this because, in the United States, there is no individual or institutional work of any moment that has not been affected profoundly by the war.

The Franklin Institute and its work have been affected in various ways. The war has taken from the Institute three of its Managers—Mr. Charles Day, chairman of the Committee on Sectional Arrangements, now, as a member of the Army War Council, doing important work for the Government; Mr. William Chattin Wetherill, chairman of the Committee on Science and the Arts, now an ensign in the Aviation Section, U. S. Navy; and Mr. Theobald F. Clark, now an artillery captain. The war has taken our Secretary, Dr. R. B. Owens, now a major in General Pershing's force; our Science and Arts Assistant, Mr. T. N. Parrish, now a lieutenant of the Signal Corps. The work of the Institute has not ceased in any department because of the absence of these gentlemen. The work of the Secretary has been taken over, and is being ably performed, by Dr. George A. Hoadley, a member of the Board; and other of the work heretofore done by members now gone to war is being covered by other members who have volunteered for the purpose. We sadly miss our absent associates; we wish them a safe and early return to the duties of civil life, and in the interim we increase our efforts to maintain the Institute in useful operation.

The Managers of the Institute, this year, as from the beginning, while conducting the routine work committed to them, have purposed to maintain for the Institute such a reputation for efficiency and for patriotism as would mark it as a potential force available to the nation in time of distress. Your Board are gratified to be able to say to you that we have the evidence of this reputation in the number of demands that the departments at Washington have made upon us since the entry of our country into war, each of which has been promptly honored.

At the request of the War Department, the Institute initiated and is now conducting a school in wireless telegraphy, with about one hundred and twenty students. These are young men subject to draft, and qualifying themselves for the operation of modern devices for the transmission of information on the battle-field. The Institute, through its executive officers, has had a part in the formation of schools of navigation and of marine engineering, now being conducted successfully in this city, and already accredited with some hundreds of graduates. These schools were started at the request of the United States Shipping Board. The School of Navigation was opened in the Institute. As requested by the War Department, we established and maintained a recruiting and examination station for applicants for admission to the aviation service. Upon Government request we have made studies of the

state of various arts concerned with the conduct of a war. Though thus called upon to undertake these emergency duties, the regular work of the Institute has progressed about as usual.

More detail of the work of the year is set out in the reports of the committees, attached hereto, and to be printed in full in the 1918 Year Book. I extract from these reports as follows:

The Library Committee, Mr. Morgan, chairman, reports additions to the Library totalling 2364. It is interesting to read in this report that among our current magazines two have suspended publication and fifty-six have been discontinued temporarily because of war conditions. The contents of the Library are given as—

Volumes, bound and unbound	71,020
Pamphlets	28,845
Maps and charts	2,888
Photographs	1,336

The committee again calls attention to the importance of binding the present unbound volumes. More or less volumes are bound every year, but there are at present some 2800 needing binding. We need more funds for this purpose. The committee reports difficulty in obtaining sufficient office assistants.

The Committee on Museums, Mr. Outerbridge, chairman, reports a number of interesting additions to our group of models and historic apparatus.

The report of the Committee on Meetings, Mr. Rogers, chairman, is a record of the stated meetings held and contains an interesting report of the presentation of the Franklin Medal, at the May meeting, to Dr. Hendrik Antoon Lorentz, F.R.S., of the Royal Academy of Sciences, Amsterdam and the University of Leiden, and to Dr. David Watson Taylor, Chief Constructor of the United States Navy.

The report of the Committee on Stocks and Finance, Mr. Forstall, chairman, contains a list of the funds held by the Institute, the receipts during the year, and the expenses of operation. I quote the last paragraph of the report entire, as follows:

"The total increase since last year in the principal of all funds amounts to $129,308.22; of which the principal items are the John H. Wahl Fund of $79,146.53, the increase of $23,615.04 in the General Endowment Fund from subscriptions received to meet the conditions of the Wahl bequest, and an increase of $10,284.32 in The Franklin Institute Building Fund. With the John H. Wahl Fund was received $9637.96 of accumulated income, and this accounts for the large surplus shown, which enabled a reduction of $7250.00 in 'Bills Payable.'"

The Building Fund has grown very little during the year. It amounts to $461,000, of which sum $209,000.00 is invested in nine buildings and lots at the corner of Race and Nineteenth Streets. (Since the close of the fiscal year covered by this report of the Finance Committee we have added another house and lot to our holdings on this site at a cost of $18,000.)

There will be no effort during the war to raise the additional funds necessary to the erection of a building better suited to our purposes. In the mean-

time this dignified old structure lacks little but in size and location of being a proper home for an institution of our character. And it has honored traditions that a new building will hardly accumulate in two generations.

In general, the financial affairs of the Institute continue to be in a satisfactory condition.

The report of the Committee on Sectional Arrangements, Mr. Day, chairman, gives a list of the twenty-one lectures delivered before the Sections—frequently in joint meetings with the Philadelphia branches of national engineering societies.

The report of the Committee on Science and the Arts, Mr. Wetherill, chairman, is a statement of the activities of the committee during the year and shows that the standards of the committee are being well maintained. Fifty-nine subjects were considered and twenty-five awards were recommended.

The Committee on Instruction, Mr. Paul, chairman, renders its annual report covering the 93d year of the Franklin Institute School of Mechanic Arts. The courses in Mechanics and in Naval Architecture were extended beyond the standard of previous sessions; the interest in Naval Architecture has naturally increased. The graduating class of 1917 contained 41 members. The total number of students enrolled was 372—an increase of twenty-one per cent. over the previous year. During the current year—not covered by this report, which is for the year 1916–17—the work of the schools has been greatly extended, and the committee's labors and responsibilities have been correspondingly increased.

The Committee on Exhibitions, Mr. Chambers, chairman, reports no activities during the year.

The Committee on Elections and Resignations of Members, Mr. Gibbs, chairman, reports the election of—

Resident members	58	
Non-resident members	57	
Associate members	8	
Life members	1	
Total		124

The resignation of—

Resident members	14	
Non-resident members	15	
Second class stock members	1	
Total		30

The death of—

Resident members	7	
Non-resident members	9	
Second class stock members	3	
Honorary members	3	
Total		22
Total of resignations and deaths		52
Gain in membership—all classes		72

Our membership grows slowly. We are not very good advertisers, and knowledge of the value of the Institute's work is not forced upon the community. We do not conduct campaigns for membership or for funds. Doubtless we will attract a larger membership when we are domiciled in a more prominent and popular location.

Members of The Franklin Institute, your Board of Managers still believe they are justified in reporting to you that the work of your Institute continues to be good. While those of your elected representatives who were of suitable age and condition have gone to meet your country's foes, those of us who are so conditioned as to be unable to make this supreme sacrifice have endeavored, in our less heroic field, to meet the new conditions and to continue the Institute as an efficient and ever-ready aid to the State, now in war, as for nearly a century in peace. This is our Institute's highest function, and it will spare no effort necessary to its full performance.

Respectfully submitted,

The Board of Managers,

WALTON CLARK,
President.

PHILADELPHIA, January 16, 1918.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of the Stated Meeting held Wednesday, January 2, 1918.)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, January 2, 1918.

MR. CHARLES E. BONINE, *Chairman pro tem.*

The following report was presented for first reading:

No. 2704.—Sweetland Filter Press.

The following reports were presented for final action:

No. 2701.—Talbot Air Lift. Recommended that the Edward Longstreth Medal of Merit be awarded to Levi Talbot Edwards, of Philadelphia, Pa.

No. 2703.—Sweetland Filter Cloth. Recommended that the Certificate of Merit be awarded to Ernest J. Sweetland, of Upper Montclair, N. J.

GEORGE A. HOADLEY,
Acting Secretary.

SECTIONS.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, December 13, 1917, at 8 o'clock, with Mr. George R. Henderson in the chair. The minutes of the previous meeting were read and approved.

A. V. Bleininger, Ceramic Chemist of the U. S. Bureau of Standards, Pittsburgh, Pa., presented a paper, entitled "Some Industrial Problems in Silicate Technology." Among the subjects discussed was the manufacture, in the United States, of refractories, optical glass, spark-plug porcelain, and glass pots of porcelain. The manufacture of such pots by moulding, with and without the use of a vacuum, was described.

Doctor Hoadley, Messrs. Henderson and Fulweiler, and others participated in the discussion. On motion of Mr. W. H. Fulweiler, a rising vote of thanks was extended to Mr. Bleininger. The meeting then adjourned.

JOSEPH S. HEPBURN,
Secretary.

MEMBERSHIP NOTES.

CHANGES OF ADDRESS.

LIEUT. COMMANDER A. W. K. BILLINGS, care of Commander U. S. Naval Forces, Paris, France.

CAPTAIN H. E. IVES, Signal Corps. U. S. R., 1023 Sixteenth Street, Washington, D. C.

DR. GUSTAV LINDENTHAL, 25 Church Street, New York City, N. Y.

MR. LAWRENCE T. PAUL, 202 Liberty Building, Broad and Chestnut Streets, Philadelphia, Pa.

MR. CARL D. ULMER, Minnesota By-Products Coke Company, St. Paul, Minn.

NECROLOGY.

John Price Remington was born in Philadelphia, March 26, 1847, died on January 1, 1918.

He was educated in the Friends' School and the Central High School of Philadelphia, and later entered the Philadelphia College of Pharmacy, graduating in 1866. In 1868 the degree of Master of Pharmacy was conferred upon him by his Alma Mater, and in 1899 the Northwestern University conferred upon him the degree of Doctor of Pharmacy.

Doctor Remington was made Professor of Pharmacy of the Philadelphia College of Pharmacy in 1874, and from 1877 to 1915 was director of its Pharmaceutical Laboratory. In 1893 be became Dean of the College, and had served in that capacity since that time. He had been a member of the Revision Committee of the U. S. Pharmacopœia since 1880, and was chairman of the committee since 1901. He acted as editor of the editions of 1890, 1906, and 1913.

He was president of the First International Pharmaceutical Congress, 1893, and a delegate to the Pan-American Medical Congress, which convened in Washington in the same year.

Doctor Remington was a member of the leading scientific societies of the world. His work, "Practice of Pharmacy," has had wide circulation. He had also acted as editor of the United States Dispensatory of 1883 and nineteen later revisions, and Lippincott's Medical Dictionary, 1897.

Doctor Remington became a member of the Institute in 1880.

LIBRARY NOTES.

PURCHASES.

BIGELOW, F. H.—Meteorological Treatise on the Circulation and Radiation in the Atmospheres of the Earth, and of the Sun. 1915.

BINGHAM, CHARLES.—Manufacture of Carbide of Calcium. 1916.

CHAMOT, E. M.—Elementary Chemical Microscopy. 1916.

Chemical Society of London, Annual Report, vol. 13. 1916.

FALES, E. N.—Learning to Fly in the United States Army. 1917.

HERING, CARL, and GETMAN, F. H.—Standard Tables of Electrochemical Equivalents, and Their Derivatives. 1917.

HIRSCHBERG, C. A.—Compressed Air for the Metal Worker. 1917.

HUGHES, C. H.—Handbook of Ship Calculations, Construction and Operation. 1917.

KENNELLY, A. E.—Artificial Electric Lines: Their Theory, Mode of Construction, and Uses. 1917.

LOWRY, T. M.—Historical Introduction to Chemistry. 1915.

OSTWALD, WOLFGANG, and FISCHER, M. H.—Theoretical and Applied Colloid Chemistry. 1917.

Thomas's Register of American Manufactures, Annual, 9th. 1917.

West Virginia Geological Survey, County Reports and Maps, Braxton and Clay Counties. 2 volumes. 1917.

ZSIGMONDY, RICHARD, and SPEAR, E. B.—Chemistry of Colloids. 1917.

GIFTS.

A. G. A. Railway Light and Signal Company, Catalogues Nos. 100 and 300; A. G. A. Highway Danger Signal; and A. G. A. Railway Grade Crossing Signal. Elizabeth, N. J., no dates. (From the Company.)

American Institute of Electrical Engineers, Transactions, 1907–1910; Indexes, 1884–1900; 1901–10. New York, 1908–13. (From Mr. Henry Beyer.)

American Pulley Company, Getting Maximum Pulley Efficiency. Philadelphia, no date. (From the Company.)

Badenhausen Company, Catalogues, Just About Boilers, and Just About Marine Boilers. Philadelphia, 1917. (From the Company.)

Besly, Charles H. & Company, Besley's Modern Disc Grinding Practice, A Treatise on the Art of Disc Grinding; and Condensed Catalogue of Grinders. Chicago, 1915, 1916. (From the Company.)

Borden Company, Catalogue No. 12, Beaver Cutting and Threading Tools for Pipe. Warren, Ohio, no date. (From the Company.)

Boston Transit Commission, Twenty-third Annual Report for the Year Ending June 30, 1917. Boston, Mass., 1917. (From the Commission.)

Budd Grate Company, Efficiency in Your Boiler Room. Philadelphia, no date. (From the Company.)

Bunting Brass and Bronze Company, Catalogue of Bronze Bushings and Bearings. Toledo, Ohio, 1916. (From the Company.)

Byers, A. M., Company, Bulletin No. 30, Genuine Wrought Iron Pipe. Pittsburgh, Pa., 1917. (From the Company.)

Canada Department of Mines, Geological Survey, Memoir 100, The Cretaceous Theropodous Dinosaur Gorgosaurus, by Lawrence M. Lambe. Ottawa, 1917. (From the Survey.)

Carlyle Johnson Machine Company, The Johnson Friction Clutch as Applied in Machine Building; and Catalogue 1915, The Bud-E Marine Motor. Manchester, Conn., 1912, 1915. (From the Company.)

Carnegie Endowment for International Peace, Year Book, 1917. Washington, 1917. (From the Endowment.)

Cook, Asa S., Company, Catalogue of Wood Screw Machinery. Hartford, Conn., 1918. (From the Company.)

Dartmouth College, The Catalogue, 1917–18. Hanover, N. H., 1917. (From the College.)

Davis, G. M., Regulator Company, Catalogue 9, Valve Specialties for the Automatic Regulation of Pressure. Chicago, no date. (From the Company.)

Duplex Hanger Company, Catalogue, Edition 17, of Duplex Hangers and Caps. Cleveland, Ohio, no date. (From the Company.)

DuPont de Nemours & Company, DuPont Products Book. Wilmington, Del., 1917. (From the Company.)

Ehret Magnesia Manufacturing Company, "85 Per Cent. Magnesia" and Heat-Insulation; and Magnesia Association Specifications for 85 Per Cent. Carbonate of Magnesia Non-Conducting Coverings for Power, Heating, and Ventilating Systems. Valley Forge, Pa., 1917. (From the Company.)

Fafnir Bearing Company, Fafnir Ball Bearings for Pleasure Cars. New Britain, Conn., 1917. (From the Company.)

Fellows Gear Shaper Company, Operator's Handbook; and Design of Splines and Clutch Teeth. Springfield, Vt., 1917. (From the Company.)

Florida Geological Survey, Ninth Annual Report, 1917. Tallahassee, 1917. (From the Survey.)

Gilbert & Barker Manufacturing Company, Catalogue of Oil Storage Systems. Springfield, Mass., no date. (From the Company.)

India Director-General of Posts and Telegraphs, Annual Report for the Year 1916–17. Simla, 1917. (From the Director-General.)

India Inspector-General of Forests, Annual Return of Statistics Relating to Forest Administration in British India for the Year 1915–16. Simla, 1917. (From the Inspector-General of Forests.)

Institution of Mining and Metallurgy, Transactions, vol. xxv, 1915–16. London, 1916. (From the Institution.)

Lagonda Manufacturing Company, Catalogue L-10, Lagonda Boiler Tube Cleaners. Springfield, Ohio, 1917. (From the Company.)

Lane Manufacturing Company, Catalogues of Equipment for Use in Wooden Shipyards. Montpelier, Vt., 1909–17. (From the Company.)

Library of Congress, Report of the Librarian and of the Superintendent of the Library Building and Grounds for the Fiscal Year Ending June 30, 1917. Washington, 1917. (From the Library.)

Lovejoy Tool Company, Inc., Catalogue of Patented Inserted-Cutter Tools. Springfield, Vt., 1917. (From the Company.)

Manchester Steam Users' Association, Memorandum by Chief Engineer for the Year 1916–17. Manchester, 1917. (From the Association.)

Moody Manual Company, Moody's Manual, vol. v, Complete List of Securities Maturing January 1, 1918, to December 31, 1919. New York, 1917. (From the Company.)

National Association of State Universities in the United States, Transactions and Proceedings, vol. 15. Grand Forks, N. D., 1917. (From the University of Kentucky.)

National Machinery Company, National Forging Machine Talk, No. 27. Tiffin, Ohio, no date. (From the Company.)

Nelson Blower and Furnace Company, Catalogue of the Stevens Under-Feed Stoker. Boston, Mass., 1917. (From the Company.)

New York Public Service Commission for the First District, Report for the Year Ending December 31, 1915, vol. i and iii. Albany, 1916. (From the Commission.)

New Zealand Department of Mines, Geological Survey, Palæontological Bulletin No. 5. Wellington, 1917. (From the Survey.)

New Zealand Minister of Mines, Mines Statements for the Year 1916. Wellington, 1917. (From the Minister.)

Norton Company, Booklet Descriptive of Tool Grinding. Worcester, Mass., 1917. (From the Company.)

Pennsylvania Commissioner of Banking, Twenty-second Annual Report for the Year 1916, part ii, Building and Loan Associations. Harrisburg, 1917. (From the State Librarian.)

Pennsylvania Secretary of the Commonwealth, Alphabetical List of Charters of Corporations Enrolled During the Two Years Beginning June 1, 1915, and Ending May 31, 1917. Harrisburg, 1917. (From the State Librarian.)

Positive Differential System Company, The "Positive" Air Return System; and Vacuum Return Line Systems. New York, no dates. (From the Company.)

Royal Society of Victoria, Proceedings, vol. xxix, parts i and ii, October 1916, March, 1917. Melbourne, 1916–17. (From the Society.)

Second Pan-American Scientific Congress, Proceedings, vol. i, section i; vol. ix, section viii, part i. Washington, 1917. (From the Congress.)

Security Insert Company, The Security Insert or Ceiling Socket for Concrete Work. Philadelphia, no date. (From the Company.)

Society of Motion-Picture Engineers, Standards Adopted by the Society, first edition. Washington, 1917. (From Mr. C. Francis Jenkins.)

Sturtevant, B. F., Company, Bulletins Nos. 222, 223, 224, 226, 227, 228, 232, 233, 237, 238, 245; Catalogues Nos. 215, 230, 235, 236, 240, 242, 244, and 248. Hyde Park, Mass., 1916–17. (From the Company.)

United Engineering and Foundry Company, Bulletin C, "United" Plate Mills. Pittsburgh, Pa., 1917. (From the Company.)

U. S. Chief Signal Officer, Annual Report, 1917. Washington, 1917. (From the Chief Signal Officer.)

U. S. Commissioner of Lighthouses, Annual Report for the Fiscal Year Ended June 30, 1917. Washington, 1917. (From the Commissioner.)

U. S. Department of the Interior, Director of The National Park Service, Report for the Fiscal Year Ended June 30, 1917. Washington, 1917. (From the Department.)

U. S. Interstate Commerce Commission, Thirty-first Annual Report, December 1, 1917. Washington, 1917. (From the Commission.)

Vermont Bank Commissioner, Annual Report for the Year Ending June 30, 1917. Rutland, 1917. (From the State Librarian.)

Western Australia Geological Survey, Bulletins Nos. 60, 63, and 66. Perth, 1915–16. (From the Survey.)

Westinghouse Electric and Manufacturing Company, Catalogue No. 30, Direct-Current Motors and Generators. East Pittsburgh, Pa., 1917. (From the Company.)

Whiting Foundry Equipment Company, Catalogue No. 132, Tumblers and Dust Arresters. Harvey, Ill., no date. (From the Company.)

Wilson Welder and Metals Company, Inc., Catalogue No. 2, Electric Welding. New York, 1917. (From Mr. W. E. Symons.)

Worthington Pump and Machinery Corporation, Bulletin D-1301, October, 1917. New York, 1917. (From the Corporation.)

Wyoming State Geologist, Bulletin No. 16, Mining Laws, Federal and State. Cheyenne, 1917. (From the State Geologist.)

Yeomans Brother Company, Bulletins Nos. S-1000, E-2000, B-3000, P-4000, and C-5000. Chicago, 1916–17. (From the Company.)

BOOK NOTICES.

THE KILN DRYING OF LUMBER, by Harry Donald Tiemann, M.E., M.F. Philadelphia and London, J. B. Lippincott Company, 1917. 316 pages, illustrations, diagrams, and tables. Cloth, 6 x 9 inches. Price, $4.

Of all structural materials in common use from time immemorial, there is none that has been applied to a greater variety of purposes or more extensively than wood, and, despite the familiarity that has been acquired with its peculiarities, there is probably no structural material whose properties cannot now be specified with a greater degree of exactness. Trees contain from 30 to 200 per cent. in water of the dry weight of the wood, and it is essential to remove the greater part of this water to make the wood serviceable. The moisture content having also an important influence upon the strength of the wood, the strength increasing with the dryness, it is highly desirable to be able to specify the moisture content of lumber within precise limits, as well as its treatment and resulting physical state.

It takes a long time for wood to become air-dry, and many woods seldom air-dry without great losses in warping, checking, case-hardening, and honeycombing. The author points out that these losses may be greatly reduced by properly kiln-drying the green material in kilns in which humidity and circulation and the temperature can be suitably controlled. The value of a technical knowledge of the kiln drying of lumber is therefore apparent, and it is the purpose of this book to present the best information available on this important subject.

The structure and properties of wood, common practices in drying, and the effects of drying are first considered. Then, passing to the main topic, the principles of kiln drying and methods of securing the necessary conditions of temperature and humidity for efficient results are analyzed in detail. Various forms of kilns in current use are described and the results obtained from them discussed at length. The work is of a very different type from that of the usual woodcraft text. The subject is presented from a consideration of fundamental principles, from which, with observations from practice, deductions are made by rational and analytical methods. While deeply interesting from a descriptive point of view, it is quite the book that will appeal to the technically trained reader who appreciates an orderly and precise method of arriving at results.

LUCIEN E. PICOLET.

PUBLICATIONS RECEIVED.

Refractory Materials: Their Manufacture and Uses, by Alfred B. Searle. 444 pages, illustrations, 8vo. Philadelphia, J. B. Lippincott Company, 1917.

Aids in the Commercial Analysis of Oils, Fats, and Their Commercial Products, a laboratory handbook, by George Fenwick Pickering. 133 pages, 8vo. Philadelphia, J. B. Lippincott Company, 1917.

Athenæum Subject Index to Periodicals, 1916, issued at the request of the Council of the Library Association. Historical, political, and economic sciences. 119 pages, quarto. London, The Athenæum, 1917. Price, 5 shillings net.

U. S. Bureau of Standards: Technologic Paper No. 95, Durability of Cement Draintile and Concrete in Alkali Soils (containing results of third year's tests), by R. J. Wig, Engineer Physicist; G. M. Williams, Assistant Engineer Physicist, and A. N. Finn, Associate Chemist, Bureau of Standards, in Coöperation with S. H. McCrory, Chief of Drainage Investigations, Department of Agriculture; E. C. Bebb, Engineer, U. S. Reclamation Service; L. R. Ferguson, Engineer, Portland Cement Association. 94 pages, plates, 8vo. Washington, Government Printing Office, 1917. Price, 35 cents.

U. S. Bureau of Mines: Bulletin 130, Blast-furnace Breakouts, Explosions, and Slips, and Methods of Prevention, by F. H. Willcox. 280 pages, illustrations, plates, 8vo. Bulletin 158, Cost Accounting for Oil Producers, by Clarence G. Smith. 123 pages, tables, 8vo. Washington, Government Printing Office, 1917.

Canada, Department of Mines, Mines Branch: Bulletin No. 16, Mineral Springs of Canada, in two parts. Part I, The Radioactivity of Some Canadian Mineral Springs, by John Satterly, M.A., D.Sc., and R. T. Elworthy, B.Sc. 60 pages, plates, map, 8vo. Ottawa, Government Printing Bureau, 1917.

United States Tariff Commission, first annual report for the fiscal year ended June 30, 1917. 26 pages, 8vo. Washington, Government Printing Office, 1917.

Concrete Highway Bridges. 27 pages, illustrations, 8vo. Concrete ships. 46 pages, illustrations, 8vo. Chicago, Portland Cement Association, 1917.

CURRENT TOPICS

The Toy Transformer and Its Hazards. C. H. THORADSON, in *Electrical Review.* (*Quarterly of the National Fire Protection Association,* vol. xi, No. 2, p. 155, October, 1917.)—Electrical transformers for stepping down 110 volts alternating current of the usual lighting circuit to much lower potential for operating electrical toys have become an established commodity. It may be said that small electrical devices used on a few volts may have no limitations as to cheapness. With the toy transformer that is connected to the 110-volt circuit it is quite otherwise, and it is of the utmost importance that toy transformers be made, as far as possible, proof against misuse.

The dangers from short-circuiting are well understood, and a number of protective devices to guard against short-circuit have been devised. The greatest danger, however, lies in the possibility of connecting the 110-volt cord to the low-voltage side of the transformer. In such a case the transformer becomes a step-up transformer, delivering a potential that can be fatal to anyone touching the secondary circuit when the current is thrown on. To determine what would really happen if a transformer is so connected, a small toy transformer that had been rated at less than 50 watts was tested with an oscillograph, showing the shape of the secondary voltage and current wave. The highest potential on the low-voltage side was in the neighborhood of 25 volts. Across the high-voltage terminals a non-inductive resistance was connected, corresponding in resistance to the body of a full-grown person. On applying 110 volts to the low-potential side, the high-voltage measured 596 volts with one-eighth ampère flowing through that resistance. The lowest secondary voltage was about three volts. When 110 volts was switched on this circuit and a corresponding resistance was connected across the high-voltage side, a potential of 1140 volts was delivered with a current of one-third of an ampère. The oscillograph showed a surge voltage superimposed on this voltage that indicated 2070 volts.

Tests of Oxacetylene Welded Joints in Steel Plates. H. F. MOORE. (*Bulletin No. 98,* Engineering Experiment Station, University of Illinois, December 10, 1917.)—A series of tests of the strength of oxacetylene welded joints in mild steel plates has been completed by the Engineering Experiment Station of the University of Illinois under the direction of H. F. Moore, Research Professor of Engineering Materials. Specimens were supplied by the Oxweld Acetylene Company of Chicago, and tests were made in the laboratories of the Station at Urbana under three conditions of loading:

(*a*) static load in tension (in a testing machine), (*b*) repeated load (bending), and (*c*) impact in tension (in a drop testing machine).

For joints made with no subsequent treatment after welding, the joint efficiency for static tension was found to be about 100 per cent. for plates one-half inch in thickness or less, and to decrease for thicker plates. For static tension tests, the efficiency of the material in the joints welded with no subsequent treatment was found to be not greater than 75 per cent. The joints were strengthened by working the metal after welding and were weakened by annealing at 800° C. For static tests and for repeated stress tests, the joint efficiency sometimes reaches 100 per cent.; the efficiency of the material in the joint is always less. This indicates the necessity of building up the weld to a thickness greater than that of the plate. The impact tests show that oxacetylene welded joints are decidedly weaker under shock than is the original material; for joints welded with no subsequent treatment, the strength under impact seems to be about half that of the material. In general, the test results tend to increase confidence in the static strength and in the strength under repeated stress of carefully made oxacetylene welded joints in mild steel plates.

Farm Reservoirs. S. FORTIER. (U. S. Department of Agriculture, *Farmers' Bulletin 828*, July, 1917.)—The main purpose of reservoirs suited to the needs of individual farmers and small groups of farmers is to store water for the irrigation of gardens, orchards, and truck farms, but they may serve also to store water for stock and to provide domestic supplies for farm dwellings. Farm reservoirs are used most commonly in conjunction with pumping plants operated by gasoline engines, windmills, or electric motors. A usual source of supply is the well, though the flow from springs, brooks, flowing wells, and small creeks is also utilized.

Water escapes from unlined earthen reservoirs in two ways other than through the outlet or wasteway. A part of the contents is absorbed by the materials forming the bottom and sides or else percolate through them, and another part is vaporized at the surface and passes off into the air. Seepage losses may be regarded as one of the most serious defects in the common practice of storing water on farms, and may be prevented almost entirely by lining the reservoir with concrete. Such a lining may cost, however, as high as 10 cents per square foot, or more than $1000 per acre-foot of water stored. Since the interest on the cost of a concrete lining might amount to more than the value of the water wasted annually, the cheaper method is often adopted of digging a trench where the centre of the embankment is to rest down to bed-rock or other good material and building therein a wall of concrete, known as a rim core wall. A clay puddle may be substituted where a concrete core wall proves too expensive. In this case a much wider trench is dug, filled with the best material available, and carefully puddled and rammed.

The customary practice in building these reservoirs is to locate them on the highest suitable ground adjacent to the pumping plant. The material for the embankments is taken from the inside, the space being first plowed and then scraped. To secure earth from the outside of the reservoir would remove the upper valuable layer of soil. Forming the banks from material taken from the inside results in lowering the bottom considerably below the natural surface of the ground and in this way lessens the effective holding capacity of the reservoir, since the water in the bottom cannot be drawn off and used in irrigation. On the other hand, there is a decided advantage in having this extra storage to stock with suitable kinds of fish.

The Quebec Bridge Centre Span in Place. ANON. (*Iron Trade Review*, vol. lxi, No. 13, p. 679, September 27, 1917.)—The work of hoisting into position the central span of the Quebec Bridge of the Transcontinental Railway over the St. Lawrence River, which was commenced September 17, was successfully concluded on September 20, when the connecting structure was bolted to the two cantilever arms. The span, 640 feet in length and weighing 5540 tons, was towed on pontoons from Sillery, where it was constructed, and was raised by eight hydraulic jacks having rams 22 inches in diameter and a working pressure of 4000 pounds to the square inch. The span was hoisted two feet at a time. The hydraulic pumps were operated by compressed air. Long mooring frames were suspended from each of the cantilevers, and huge pins were inserted into the frames at every two feet to sustain the structure until the next lift.

It will be some months before the bridge is ready for the passage of trains. The painting of the structure will occupy about three years. When complete, the bridge will shorten the railway trip between Halifax and Winnipeg by half a day. The cost of the bridge will be between $18,000,000 and $20,000,000. Its total length is 3239 feet, and the distance between the piers on which the cantilevers rest is 1800 feet. The height of the central span above the water is 150 feet. Each of the cantilever arms is 562 feet in length, and the total weight of steel, when everything is in place, will be about 65,000 tons.

The building of the bridge was commenced in 1906. The design then adopted provided for the extension of the cantilever arms until they met in the middle. In 1907 one of the arms collapsed, causing a loss of 70 lives. A new design then was adopted with a central span to be floated on pontoons and hoisted into position. The first attempt to carry out this plan resulted disastrously last year, when the hoisting apparatus broke and the span fell into the river, with a loss of 14 lives. The financial loss entailed by these catastrophes was about $8,500,000.

Phosphorescent Zinc Sulphide. E. MACDOUGALL, A. W. STEWART, and R. WRIGHT. (*Journal of the Chemical Society* (London), August, 1917, through the *Illuminating Engineer*, vol. 10, No. 9, p. 238, September, 1917.)—It seems to be recognized that zinc sulphide in the phosphorescent form can be obtained only by the action of heat. Ordinary precipitated zinc sulphide shows no sign of phosphorescence. By the application of heat, however—that is, by deflagrating a mixture of zinc and sulphur—the desired property may be produced. In carrying out this process, the temperature is of considerable importance. Below the region of 650° C. even prolonged heating produces only a poor phosphorescent effect. Between 650° and 900° the results are much better, while heating for a considerable time above 1100° again produces very poor specimens. The material produced below 650° is viscous and amorphous, that obtained between 650° and 900° semicrystalline under the microscope, and that produced at 1100° purely crystalline. It appears, therefore, that the semicrystalline state is a desirable condition to produce phosphorescence; the best samples were obtained by heating to some temperature for a time not exceeding an hour and a half. The temperature has also an effect on the nature of the after-glow. Specimens produced at 650° give blue phosphorescence, while higher temperatures lead to greens and even yellows.

The effect of impurities, such as iron, is prejudicial, even if present in minute quantity; others, such as sodium chloride, increase the phosphorescent effect. The addition of manganese, again, gives rise to a marked golden-yellow phosphorescence, and manganiferous zinc sulphide exhibits strong tribo-luminescence (*i.e.*, production of light on friction). In conformity with what appears to be the experience of other observers, the results obtained by radium stimulation do not in any way concord with those obtained by stimulation with light. One interesting fact is that the phosphorescence of a prepared sample of zinc sulphide may apparently be much diminished by washing with water. It therefore appears that some material soluble in water is necessary to good phosphorescence, and further evidence on this point is furnished by the fact that the conditions of precipitation have an important bearing on the quality of the product. It may be suggested that good phosphorescent effect is associated with the presence of a skin of zinc chloride over the sulphide, producing a condition of strain. This substance would be washed out by water and its removal might cause the diminution in phosphorescence brought about by washing.

The Status and Prospects of Gas Lighting. W. J. SERRILL. (*Transactions of the Illuminating Engineering Society*, vol. 12, No. 7, p. 292, October 10, 1917.)—A lack of uniformity in the fuel delivered to the burner is the first obstacle to good gas lighting. It does not follow that only one quality or kind of gas should be made all over the country, but rather that, when burners are once adjusted and in

use, it is highly desirable that the fuel thereafter fed to them be kept uniform. In the past principally two kinds of gases have been general—coal gas and water gas—but in recent years coke-oven gas has become an important factor. These gases differ from each other in gravity, in heating power, and in air requirement, and under these conditions a desirable uniformity in the gas has not been easily maintained. The effort to maintain a standard of candlepower as the criterion of the quality of the gas, now happily in process of abandonment, has been the principal cause of variability in the other qualities. As an index of the quality, candlepower is useful only in an open-flame burner. It has no value in the incandescent gas burner; on the contrary, the effort to maintain it introduces effects that are detrimental to incandescent gas lighting, and by common consent the gas industry is abandoning the candlepower standard in favor of the heat-unit standard.

To variations in pressure are due many of the causes of dissatisfaction with gas burners. The demand for uniformity by the incandescent gas burner is not, however, completely met by the unbroken delivery of gas of uniform quality; this uniform gas must come to the burner under constant pressure. Strictly uniform pressures are possible only on high-pressure systems with a governor on each service. Pressures approaching this ideal of uniformity may be obtained on low-pressure by utilizing a system of feeder mains, or a belt line provided with governor stations located so as to feed into the distribution system at various points.

Maintaining a uniform gas at the burner is not the only benefit derived by the abandonment of the candlepower standard; an additional advantage lies in the smaller quantity of condensable hydrocarbons in the gas, with a diminution of the tendency to cause smoke by the clogging of orifices in the burners and the darkening of walls and ceilings. Second only to the objection of discolored walls and ceilings, if not indeed of equal importance, are the problems of ignition and distance control. These have to do with the factor of convenience, an attribute of prime value, and are recognized as problems of fundamental importance. Mechanical and chemical inventiveness have accomplished much toward their solution, and there is reason to believe that the end has been reached.

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